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Mechanical Properties of Solvent Cast Graphene-Polymer Nanocomposites

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COLLEGE OF WILLIAM AND MARY CHEMISTRY DEPARTMENT

Mechanical Properties of Solvent Cast Graphene-Polymer Nanocomposites

by Joseph D Christesen

A thesis submitted in partial fulfillment of the requirements for a degree with Honors in Chemistry
from the College of William and Mary in Virginia

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Abstract

Polymer nanocomposites were prepared using a solvent cast technique with various polymers were dissolved in solvents and dried into a flat film adding graphene as the nanocomposites. Graphene, a material that is ten times stronger than steel, was used in an attempt to create light yet strong materials for application in airplane and car bodies. Polyethylenimine (PEI) was dissolved using dimethylacetamide (DMAc) and polystyrene (PS) was dissolved using dimethylformamide (DMF). Graphene was exfoliated in DMF and added to each polymer/solvent mix in varying concentrations. The solvent mix was then spread out onto glass to create nanocomposite films. The films were then dried so each had the same solvent content. It was noticed that there was a positive relationship between the graphene concentration and the maximum stress, elongation at break, and the modulus of each material creating a material that is stronger, more flexible, and lighter.

Table of Contents	1
Introduction	2
Background	3
Nanocomposites	5
Graphene	6
Graphene Oxide	7
Solvent Casting	8
Experimental	9
Polymers	9
TGA	9
Tensile Testing	10
GO Production	11
Vacuum Oven	11
Results	12
Solvent Content	12
Exfoliation/Dispersion	16
PEI	17
Polystyrene	19
Conclusion	22
Bibliography	23
Appendix	24

Introduction

Materials are an important facet of human life and societal progress. Clay was used at the beginning of societal development as a way of storing food and water. Its ability to be molded into a variety of shapes along with its strength, ease of acquiring the material, and ease of production made it an ideal container. However, its brittleness made it a less than ideal material for either weaponry or armor. Other materials such as steel, glass, and concrete have all lead to significant technological development and progress. Steel was a main part in the technological advancement of the Industrial Revolution, glass is a main staple for chemistry labs the past century, and concrete is extremely strong against compressive forces which has made it a staple in building construction.¹ Recently plastics have become the material from which new technologies have flourished. Plastics are an extremely common and are used in everything from piping to containers to computer parts. The invention of plastics has opened the door for many new technologies, and now plastics are being used to create a new type of material: nanocomposites.

Each of these materials has a strength which had made it a useful material, but all of them have a weakness or weaknesses. Clay is very brittle, steel is extremely dense, glass is brittle, concrete is weak against tensile forces, and plastics are not very strong. Attempts to alleviate these problems were made with different processing techniques and combining the materials into composites in order to combine the greatest strengths of each material.² Steel is added to concrete as rebar in order to lend concrete its strength against tensile forces while creating a lighter material than just pure steel. While composites tend to have better mechanical properties, they also have their drawbacks. They required very high loadings, failures tend to be catastrophic, and they can be very costly.

The approach that most researchers have taken to recently is nanocomposites. Nanocomposites address the main problems of composites in that they operate at fractional loadings of normal composites, they can suffer cracks but not fail, and they tend to be very cheap. Different nanomaterials have been developed with mechanical properties better than those of steel. Some nanomaterials include clays, metal-ion complexes, carbon nanotubes, and graphene.³ These materials promise a future of super materials that are light, cheap, and strong. However, one material has shown promise beyond all of the others with its extremely high modulus and low price, graphene is the future material for nanocomposites.

Background

Testing the mechanical properties of materials has its own set of vocabulary and definitions which will be important to discuss before proceeding further. One of the most basic mechanical tests is a simple tensile test where tension is applied along the long axis until failure of the material, and stress is plotted versus strain. Though this is the basic mechanical test, it produces a lot of very important data. Stress is defined as the force being applied to a body divided by the cross sectional area before any force is applied as in equation 1.1, and strain is defined as the change in length along the long axis divided by the original length along the long axis as in equation 1.2. The plot of stress versus strain gives information about the strength, toughness, and modulus of a material that becomes very important in characterizing the mechanical properties of the material.

Tensile strength, σ_{ts} , is quite simply the amount maximum stress that can be sustained by the material in tension.⁴ This is an important measure of how much energy or force a material can sustain before either undergoing irreversible deformation, the yield strain, or fracturing, the ultimate strain which is very important to the usefulness of the material. The toughness of the material is defined as the area under the stress-strain curve up to the point of fracture with units of energy per unit volume of

material.⁴ This can also be defined as a material's resistance to fracture. The Young's modulus, E, or tensile modulus, is a very important measurement for the characterization of a material. It is defined as the change in strain, ϵ , over the change in stress, σ , in equation 1.3 and can be more easily described as the slope of the stress vs. strain plot. This characterizes the material's ability to withstand tensile stress, σ , related to its elongation, ϵ , or deformation. This can also be thought of as the stiffness of the material or its resistance to deformation.⁴

$$\sigma = \frac{F}{A_0} \quad \text{Stress} \quad (1.1)$$

$$\epsilon = \frac{l_i - l_0}{l_0} = \frac{\Delta l}{l_0} \quad \text{Strain} \quad (1.2)$$

$$E = \frac{\sigma}{\epsilon} \quad \text{Young's Modulus} \quad (1.3)$$

Tensile testing is not the only form of mechanical testing a material. Stress may be applied to the material in shear mode. This is where two forces are applied to the material parallel to the upper and lower faces. The equation for shear stress is the same as tensile strain equation 1.1 except shear strain is referred to by τ . A form of shear stress that is used is torsion testing. This is where a rotational motion in the material is produced about the longitudinal axis of one end of the material relative to another end.⁴ This turns out to be another useful technique in the qualification of a material.

With tensile testing, a material is stretched until it fractures. Therefore, it is important to understand the mechanics behind the fracturing of a material and especially how it relates to nanocomposites. Any fracture process involves two steps: crack formation and propagation.⁴ The crack formation occurs due to pockets forming from the stretching of the material. The material is not able to hold onto itself anymore, and gaps form in the material. These pockets then coalesce into larger pockets with crack propagation. From there the crack continues to grow outward until it reaches the edge and there is a catastrophic failure of the material. One of the advantages of nanocomposites is the

ability to restrain these catastrophic failures. Randomly oriented nanocomposites will have the crack propagation stopped by the stronger filler. This is due to two facts. First, the filler is much stronger than the matrix so it will be able to resist the greater forces of the crack propagation. Second, nanocomposites are randomly oriented throughout the material so the pseudo random walk of the crack propagation will likely run into a filler particle which would stop the crack propagation due to the first reason.

It is also important to understand how a polymer responds to tensile forces. Polymers exist in several different forms from glassy to semi-crystalline to cross linked. Each one of these terms gives details about how the polymer is arranged, and how it will interact with itself. In each of these cases, the polymer can be somewhat folded up on itself. Therefore, it is possible that while under tensile forces the polymer strands can unwind somewhat which normally describes why plastics can be stretched. It is after this possible unwinding that fracture will tend to occur.

Nanocomposites

A nanocomposite consists of two parts: the matrix and the filler. The filler is the nano in the nanocomposite. This means it is a nanometer sized material as well as a very strong material loaded into the matrix at some filling fraction which can be based off of several different forms of measurement, but the most common unit used and the one that will be used in this paper is percent weight. The matrix is the material that provides the backbone of the material and the grip for the filler to grab on to. It also tends to make up the majority of the nanocomposites.

When looking at the change in the mechanical properties of nanocomposites, two factors are critical in determining the change. The first is the mechanical properties of the filler. When comparing a system that does not have filler in it, also called the neat system, and a system that has filler in it, also called a loaded system, the change in mechanical properties is going to be highly dependent on the

mechanical properties of the filler added. The stronger the filler the more potential it has to significantly increase the strength of the matrix. However, this potential may not be fully realized if the interaction between the matrix and the filler is not strong. If one were testing a nanocomposite in tensile mode, the matrix would stretch in a way that is similar to the neat system except that it can transfer load to the stronger filler.

The second factor in determining change of mechanical properties would be the interface between matrix and filler. The interaction between the matrix and the filler is critical to the mechanical properties of the system because it is the interfacial adhesion that determines the amount of stress that can be passed from the matrix to the filler.⁵ It is believed that a weaker interfacial adhesion would lead to a weaker overall material because the matrix cannot grip the filler as well, but it is also possible that slipping between the matrix and the filler could allow for a release of built up stress. That release of stress could allow the material to undergo some strain in order to get to a higher stress at break. Though this is possible it is more widely accepted that a higher interfacial adhesion would give a stronger material.

Graphene

Graphite is a very common material, and it is used in a variety of application from pencils to lubricants. It has been used since the 4th millennium BC, but the potential of using it in a nanocomposite was not truly discovered until the second half of the 20th century. Graphite is made up of sheets of sp^2 hybridized carbon atoms stacked on top of one another which are held together by van der Waals forces. It is these weak van der Waals forces which make graphite a very soft material as well as a good lubricant due to the sheets being able to slide over one another easily. However, the individual sheets of the sp^2 hybridized carbons called graphene sheets house an incredible strength.

Graphene sheets are atomically thin yet are incredibly strong. The tensile modulus of graphene is 1.1 TPa⁶ or about 160 million psi or over 10 million atmospheres. This far and away exceeds the modulus of other materials such as steel is only 200 GPa⁷. Though graphene has this incredible property, there are a few problems with processing it efficiently so that it can be used in nanocomposites. The first is that it is incredibly hard to separate the graphene sheets from graphite. This may be hard to believe as previously it was said that the interactions between the sheets was extremely weak. Even though the interactions between graphene sheets are extremely weak, the interactions are so numerous that it requires massive amounts of energy to break all of them up. Even when the sheets are separated in quartz tubes at temperatures of over 1000°C, the yield is incredibly low.⁸ The second reason is that graphene will not dissolve in any solvents because it is extremely hydrophobic and non-polar –so much so that even non-polar solvents have a hard time dissolving it. This is a big problem when trying to add it into nanocomposites in large quantities.

Graphene Oxide

The answer to the problem of processing graphene is graphene oxide (GO). GO is a form of graphene in which imperfections are added in the form of hydroxide groups or ether groups usually in a 2 to 1 carbon to oxygen ratio. These groups though weakening the overall modulus of graphene make it easier to process. The hydroxide and ether groups stick out from the 2-D plane of graphene, and this then causes the spacing between adjacent graphene sheets to go up. This extra spacing between the sheets lowers the van der Waals forces between the sheets since they are further apart so that it requires less energy to break up the new GO sheets. Now it is possible to separate the GO into single sheets. This is accomplished via a horn sonicator which creates high pressure shock waves which knock the sheets apart.

Along with the relative ease of producing GO as opposed to pure graphene, there are a few other advantages. With the addition of so much oxygen, the GO tends to be a somewhat polar

compound, and thus it is able to be dispersed in water as well as polar organic solvent called dimethylformamide (DMF). This allows the GO to be used in the solvent cast process and incorporated into polymer films.

With these advantages, there is still a disadvantage to using GO as opposed to pure graphene. Due to the added stress on the carbon-carbon bond the oxygen groups, the carbon-carbon bonds in GO are not as strong in the ones of pure graphene. This means that GO will have a lower tensile modulus than graphene. The modulus of graphene oxide has been measured to be around 0.2 TPa⁹ which is around 5 times lower than that of pure graphene. However, it is thought that the oxygen groups will give the GO a better interfacial adhesion between the polymer and itself than pure graphene. This could be due to the hydrogen bonding sites that the added oxygen groups give along with the fact that pure graphene does not have something for the polymer to “hold onto.”

Solvent Casting

Since GO is able to be dissolved in water and DMF, it is now possible to look at solvent casting as a technique for creating the nanocomposites. Solvent casting is a technique for creating polymer films in which polymer pellets are dissolved into solution, and then poured onto a glass plate where is then dried into a flat sheet or film. Solvent casting has some distinct affects on mechanical properties of the polymer.

When using the solvent casting technique, solvent tends to remain in the films to some extent even after drying. This residual solvent acts as a plasticizer for the polymer. A plasticizer can be thought of as a softener as it increases the plasticity or fluidity of the material. This has very noticeable effects on the modulus of materials. For the polymers, a small amount of plasticizer increases the modulus to a certain point from which the modulus will decrease significantly. A change in solvent content of as little as 1% can change the modulus as much as 240 MPa. This is a major concern when trying to compare the

modulus of a neat system to that of a loaded system as, unless the two have the same solvent content, they will be almost impossible to compare.

Experimental

Polymers

The polymers that were used for the nanocomposites were polyetherimide (Ultem 1000 received from Robert Orwoll's Lab) and polystyrene (Aldrich, M_w 230,000, CAS 9003-53-6). Both PEI and PS are very common thermoplastic, glassy polymers. They were chosen due to the fact that both have been very widely studied and are very common. Thus mechanical properties would be better defined than less studied polymers. They were also chosen because they are high molecular weight thermoplastic polymers. When working on the nanoscale, it was determined that creating a successful system would be more likely when working with a glassy polymer as opposed to a semicrystalline due to the size of the interactions. With a semicrystalline polymer, there are regions in the polymer which are crystalline and others which are amorphous. Therefore, it would be hard to understand the interactions of the filler with the polymer since it would be unknown whether or not the filler would be interacting with the crystalline or amorphous regions of the polymer.

TGA

Thermogravimetric analysis (TGA) is the way in which the solvent content of polymers is measured. A TGA in its most simple form is a balance that is temperature controlled. It consists of a pan suspended by a hook which is able to accurately measure the mass of the pan and its contents. There is also a sleeve that covers the pan and the hook to give an isothermal environment in which the mass measurements will be taken. The TGA can then be temperature programmed in order to see weight change relative to temperature change. This is very important in determining solvent content in

polymers. Polymer pellets from both PEI and PS will show no mass loss at temperatures around 200 °C which is well above the boiling point of any solvent that will be used. Therefore when the temperature is programmed to above the boiling point of both solvents and yet below the point where the polymer will degrade, the solvents will boil off of the polymer, and the associated mass loss will be due to the loss of solvent. That will then give the percent by mass of the sample that was solvent. This is a very accurate measurement and can give percent mass loss to a hundredth of a percent.

It is important when preparing the TGA to make sure that nothing on the pan will cause a change in mass besides the material being studied. Thus the pan is made out of platinum such that it will be resistant to very high temperature without mass loss. However to clean the pan, one cannot use any solvent or liquid for that matter as it is possible that some may remain when running the TGA, and even a small amount of change in weight can throw off the curve. Instead, a flame is used to heat the pan and everything on it to temperatures far exceeding the one in the TGA that everything has already gone through all of the mass loss. This ensures that the only source of mass loss will be due to material. Also to get an accurate percent weight loss for the material, the pan after being in the flame is placed in the TGA, and that mass will be discounted when the sample is actually run.

The temperature program was done under nitrogen gas. It started with a temperature jump to 115°C followed by a twenty minute hold. Then there was a temperature jump to 170°C where it was held for two hours.

Tensile Testing

The tensile testing machine used for these experiments consists of two grips which are separated at constant rate by pneumatic pumps. The top grip remains stationary while the bottom grip moves and exerts the force on the sample. There are then force sensors which determine the force on the upper grip. The displacement of the bottom grip is measured to give the strain on the material.

There is also a special shape which the sample must be in to get accurate data. The shape consists of two thick tabs at either end which slope into a thinner center. This shape is called a dog-bone due to its resemblance to an actual dog bone.

GO production

The graphite oxide (GO) was prepared by the Hummers method.¹⁰ First, 4 g sodium nitrate (Fluka, St. Louis, MO, purum p.a., ≥99.0%) were added to 184 mL sulfuric acid (Fisher Scientific, Pittsburgh, PA, Certified ACS Plus, 96.1 wt%) and stirred until completely dissolved. Natural flake graphite (Asbury Carbons, Asbury, NJ, Grade 3243, 99.5%) was added under vigorous stirring to avoid agglomeration. The solution became dark. After the graphite was well dispersed, 24 g of potassium permanganate (Fisher Scientific, Pittsburgh, PA, Certified ACS, 99.7%) were added slowly under stirring. CAUTION: During this process, the temperature can rise rapidly, creating severe effervescence. We added the permanganate slowly enough to keep the temperature below 100 °C. The suspension became thicker, turning into slurry. The color turned from black to dark brown. After completion of the reaction, we allowed the slurry to cool down. Then, we slowly added 400 mL of de-ionized water to the still very acidic solution, leading to an increase of temperature. After the temperature decreased to room temperature again, 80 mL of 10% hydrochloric acid (prepared from 37% hydrochloric acid, Fisher Scientific, Pittsburgh, PA, Certified ACS Plus) and 200 mL of 3% hydrogen peroxide were added to reduce the residual permanganate and manganese dioxide. The GO slurry was still strongly acid and was washed using de-ionized water repeatedly until the pH value was almost neutral. The GO slurry was then filtered to obtain GO paste. The dried graphite oxide was obtained by heating the GO paste to remove residual water.

Vacuum Oven

The vacuum oven used was a simple oven that was set up to be gas tight. It was hooked up to a turbo pump that along with the vacuum oven can remove over 30 in Hg of pressure from the oven. This

is the vacuum under which all of the samples were run. The gas pumped out of the oven was then run through a liquid nitrogen trap to prevent the solvent from entering the pump and ruining the pump. Any excess gas that was not caught by the trap was then pumped into a hood.

Results

Most of the time and effort in this project went into the creation of the polymer films for testing. It required being able to dissolve the polymer in solution along with GO while keeping the solvent content as low as possible and preventing water from getting into the system. Several methods were attempted to try to combat these issues before correct solutions were found.

Solvent Content

The first problem that was dealt with was the problem of how to keep water out of the system. This turned out to be a very difficult problem as the humidity tends to be high in Williamsburg with the average humidity hovering around 60%. The problem with getting water into the system was that the water would turn the solution an opaque white due to the water's interaction with the DMF. Then while drying, the film retains its opaque nature, but the water and DMF leave the system and leave holes in their wake. This makes the film a foam-like material and affects the mechanical properties a great deal. During the tensile testing, the stretching causes the bubbles in the film to stretch while very little stress is actually being applied to the material itself. This will cause very high elongation at break with lower stress at break

The first attempt to combat this problem was to use a dry box with just house air passing over a desiccant then being piped into a box containing the polymer film on a glass plate. There were several problems with this procedure. The first was that while the film was setting the air passing over it would cause ripples in the film making it unusable for mechanical testing. This is because there would be a very high variance in the thickness of the film as well as any unknown complications due to the film not

setting in the same manner each time thus. The second problem was the house air was so saturated with water that the desiccant would be saturated within a few minutes and be unable to absorb any more moisture.

The next attempt was to use a vacuum oven. This was first used by placing the film as soon as it was poured onto the glass substrate and pulling a vacuum on it. While this attempt worked very well on both keeping water out due to the film being in a closed system as well as keeping the solvent content low from pulling a vacuum on it, the film tended to have very large bubbles in it. This was caused by both the volatility of the solvent and the lack of gas permeability of the nanocomposite. The nanocomposite then ended up having large pockets of gas bubble up and then collapse leaving large empty pockets inside of it. The film was then unusable for mechanical tests as there were still empty pockets in the material.

The final attempt was placing the freshly poured nanocomposite into the vacuum oven at a slightly elevated temperature with no vacuum being pulled and the vent open. The elevated temperature varied between systems because it has been shown that GO can be reduced at high temperatures in polymers¹¹ so the loaded systems tended to be dried at 50 °C whereas the neat systems were dried at around 100 °C. With the elevated temperature and the confined enclosure, the solvent evaporated until it saturated the air in the vacuum oven. It would then steadily flow out the small vent opening allowing more solvent to evaporate from the film while preventing water in the atmosphere from flowing back into vacuum oven. The first part of the drying process lasted only overnight until the film solidified from which point there would be no chance of water getting into the system though there was still solvent mobility in and out of the system.

This leads to the second problem in making the films of how to keep the solvent content low. The solvent plays an important role in the modulus and overall mechanical properties of the system

because it acts as a plasticizer and softens the material. In fact as little as a 2% change in solvent content could mean a difference in modulus of as much as 20%. Therefore it is very important to monitor solvent content and make sure it is consistent as possible between systems. For the systems tested the goal was to keep the solvent content around 4%. This number was chosen for two reasons. The first is that at really high solvent concentrations (i.e. greater than 10%) the material tends to be too soft to work with and the modulus values tend to be in the tens of MPa as opposed to the GPa range. This makes comparisons between two values harder as the noise from the instrument is too large to pick up on the changes in stress. The second reason is that it would take too long to dry the sample to 0% solvent concentration at which it would also become too brittle to work with. By looking at relationship between solvent concentration and drying times, it was determined that 4% would be the right mix between drying time and softness to get a high modulus without being so brittle it would break while trying to load the sample into the tensile tester.

To dry the neat PEI sample under vacuum at 100 °C, it took around 2 weeks to get the solvent content to the acceptable level as seen in Figure 1. It was also noticed throughout that a logarithmic fit to the curve was able to predict the solvent content throughout the drying process. In a low level attempt to understand why this is the case, looking at the differential equation would be the place to start. The differential equation for the trend line to be of logarithmic form would be $\frac{ds}{dt} = -e^s$ where s is the solvent concentration and t is time. At first the eye test shows that this is at least a plausible differential equation. As the solvent content is higher the rate at which the solvent content is decreasing is much higher and as the solvent content decreases the rate at which it is decreasing will slow which agrees with the graph above. It also makes sense that the differential equation is not the simple $\frac{ds}{dt} = -s$. This is because as the solvent evaporates from the film it can only evaporate from the surface, and if the solvent does not flow through the nanocomposite instantaneously, then a gradient

would form in the film. This means that the change in solvent content would be related to the solvent content at the surface not the solvent content throughout the entirety of the film. At least at a base level the proposed differential equation makes sense, however a much more in-depth study of the theory of polymer solutions would need to be used in order to determine the exact one.

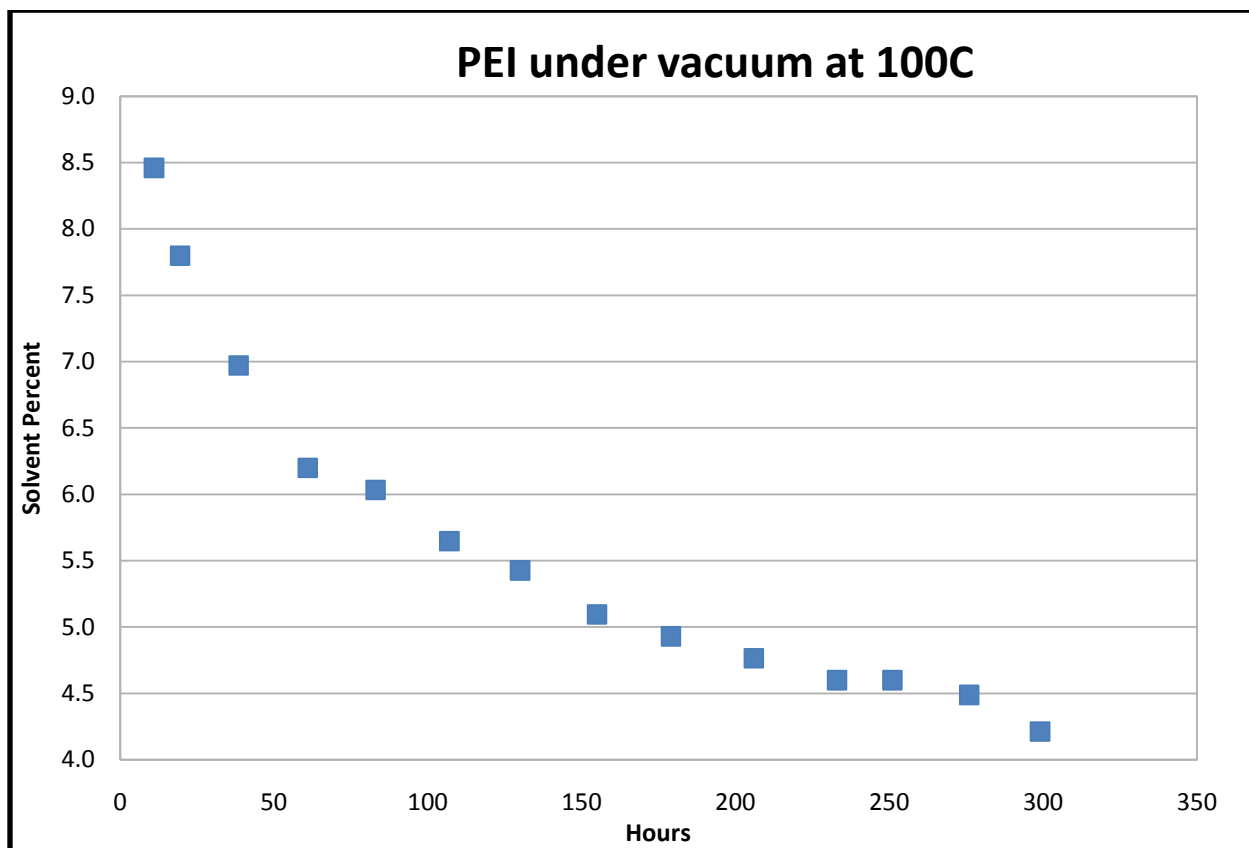


Figure 1 This is a graph of the solvent percent of the neat PEI system versus time in a vacuum at 100⁰C

To keep the drying time of the films to a minimum, it is important to limit the amount of solvent that is present at the start of film casting process. Limiting the solvent content also has another important purpose in the pouring of the films. To get good dog-bones out of a film it is important to have around 0.3 mm thick film, and to obtain this thickness it is important to have a more viscous material than a very watery solution. Therefore limiting solvent is a priority, and the two sources of solvent in the solvent casting process are from dissolving the polymer and the dispersion of the GO. The

only way to decrease the amount of solvent used to dissolve the polymer would be to increase the temperature which could then possibly reduce the GO. Then that leaves the dispersion of GO.

Exfoliation/Dispersion

Originally, the maximum concentration for a high quality dispersion of GO in DMF was only 0.5 mg/mL. That meant that for a 0.1% loaded system with 10 g of polymer, 40 mL of solvent would be used along with 20 mL of a 0.5 mg/mL solution of GO in DMF. Therefore one third of the total amount solvent used is due to the dispersion of GO. So naturally this was the place to try to start cutting away solvent content. The first attempt was just to increase the sonication time as to break up more of the clumps into single layer sheets. However after a few tests it was apparent that after a certain point the horned-tip sonicator was not breaking up the remaining clumps in the solution.

The next attempt was similar but ended up being far more effective. In the second attempt, the GO was first exfoliated in a low concentration to make a quality dispersion using the previous methods. Afterwards, the slurry was dried in the vacuum oven under a vacuum at room temperature. This pulled off all of the DMF from the slurry and what remained along the sides of the beaker was a thin film of GO. This GO film was then scrapped off of the sides and then reweighed and placed back into a DMF solution. The same procedure was used as before to try to disperse the GO in DMF, and what was found was that the GO that had been exfoliated then dried and then dispersed could reach concentrations of 4 mg/mL. This is an eight fold increase from the previous method with only a slight change in the procedure.

The exact reason for the increase in concentration is still unknown and would require more testing, but there are a few ideas as to why this would be the case. The first highlights the difference between exfoliation and dispersion. Exfoliation is the process of separation many GO sheets from one another where as dispersion is the process of evenly spreading out the single layer GO sheets

throughout the solution. Thus in the first attempts, exfoliation and dispersion were attempted in the same step. In the later attempts, exfoliation was done in a separate step from dispersion. In this way, it could be possible that after the first step exfoliated the GO sheets, the sheets would recombined, but not in an orderly manner as before thus making it easier to disperse them during the second step. The other theory that was proposed is that like the previous theory in that exfoliation and dispersion occur in two different steps. However instead of the sheets coming into random ordering, it could be possible that during the drying process that not all of the solvent evaporates, but instead some of it becomes trapped in-between the GO sheets. This makes the gap in-between the sheets even large for the dispersion in the second step making a higher concentration possible.

PEI

So with the two main problems in film creation solved, the mechanical properties of the systems could be measured. The first system to look at is PEI with three different loadings of 0%, 0.05%, and 0.1% GO. The 0% loaded or neat system gave a good idea of how the solvent casting process turned out against normal melt cast procedures. The normal modulus for PEI formed by melt cast procedures is usually around 3 GPa¹² where as the modulus obtained from the solvent casting process is around 1.8 GPa. This at least makes logical sense as the solvent within the polymer films acts as a plasticizer which makes the films softer. The softer material would then have a longer percent elongation at break which would in turn make the modulus for the material lower. So the PEI made from the solvent casting process could be simply thought of as a softer version of the melt cast one.

Even though there is a relation between the solvent cast films and normal melt casting, the real importance is in the comparison of the different loaded films with one another. As Figure 2 shows there is an increase in the modulus between all loadings as the amount of GO increases. This is a very good indicator that the GO is having some effect on the mechanical properties of the material. The GO was able to increase the modulus by 10% with only a 0.1% loading. However the 0.05% loading did not see

the same scale of increase, but it did see a slight increase even though it was within the error bars of the neat system.

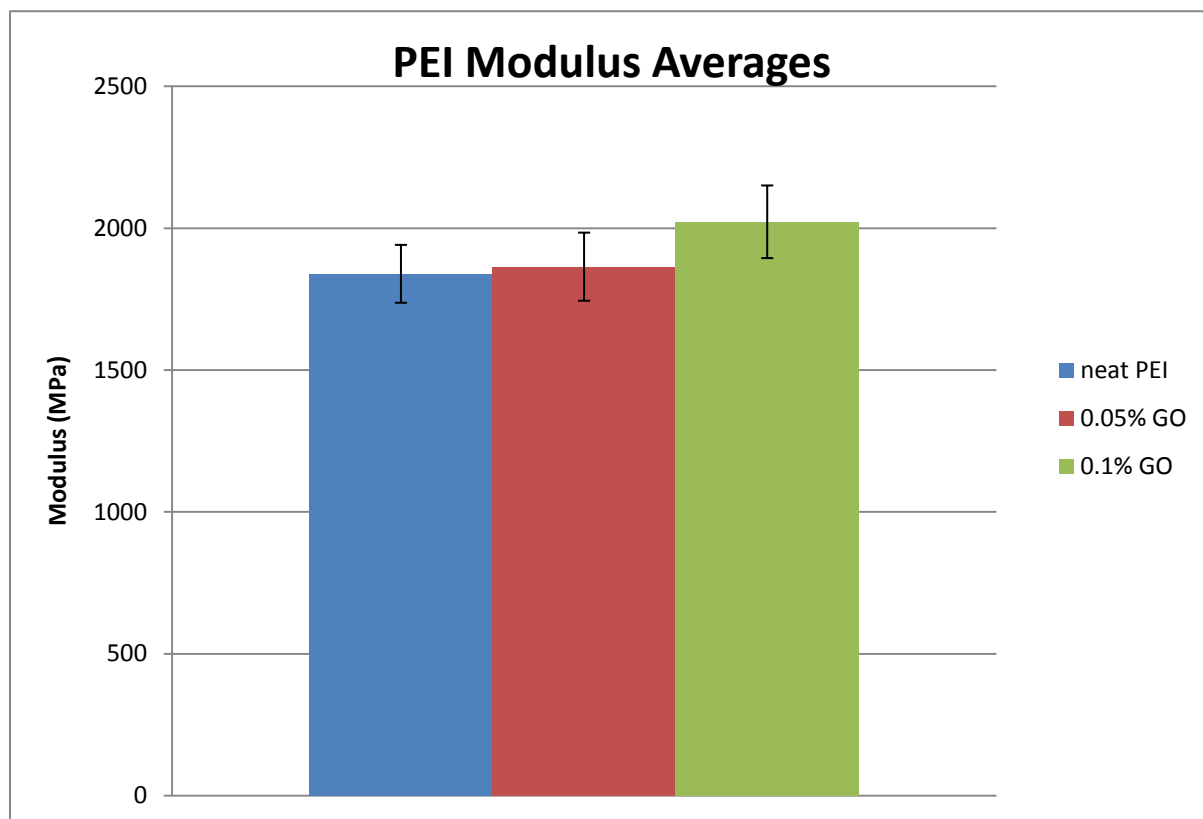


Figure 2 This is a graph of the moduli of the neat PEI system, the 0.05%, and the 0.1% loaded GO in PEI systems with error bars

One of the important things to note about this system is how both the elongation at break and the stress at break changes between each loading as seen in Table 1. In the 0.05% loaded case, both the elongation at break and the stress at break both go down by a noticeable amount. While it would make sense that GO would limit the elongation of the material, it would also make sense for the stress to go up as GO is a strong yet stiff material. However, the reason for the change in stress and strain is more likely the cause of the drop in solvent content by 0.3%. It seems to be the solvent content affected both the stress and strain at break, and therefore, see a drop in both while the modulus seems to be unaffected by a noticeable amount.

	Modulus (MPa)	Elongation at Break (MPa)	Stress at Break (MPa)	
neat PEI	1927	5.23	100.75	
neat PEI	1934	5.35	92.76	
neat PEI	1689	5.43	88.41	
neat PEI	1791	5.85	101.03	
neat PEI	1852	5.75	100.37	
Average	1839	5.52	96.66	4.2% solvent
Standard Deviation	102	0.27	5.76	
0.05% GO	1998	4.41	82.87	
0.05% GO	1767	5.10	84.71	
0.05% GO	1826	4.34	92.38	
Average	1864	4.62	86.65	3.9% solvent
Standard Deviation	120	0.42	5.04	
0.1% GO	2194	3.79	82.58	
0.1% GO	1957	5.89	103.88	
0.1% GO	2040	5.09	106.15	
0.1% GO	1898	5.78	96.24	
Average	2022	5.14	97.21	4.2% solvent
Standard Deviation	128	0.97	10.64	

Table 1 Shows the modulus, elongation and stress at break for the three PEI systems along with solvent content

For the 0.1% loaded system, the solvent content remains the same so any changes in the stress or strain at break need to be attributed elsewhere. In this case, the strain or elongation at break decreases while the max stress goes up. This goes along with what would be expected from adding a stiffer material. The stiffer GO should lend its properties in such a way that the nanocomposite exhibits properties more similar to the filler. As the PEI is strained, it will eventually start transferring the stress to the GO. The GO sheets will then be taking on most of the stress such that the overall material will undergo very little strain but will be able to take on a lot more stress. Also as the GO takes on more of the stress, it is more likely that the polymer will not be able to unravel as far which would then make the total strain lower than that of the neat polymer system.

Polystyrene

For the next system tested using Polystyrene, a general increase in modulus is seen that is similar to that of PEI. There is a slight decrease in the modulus of the system with 0.03% loading,

however the decrease is well within the error bars of the neat system so there is little statistical significance in the decrease. The increase seen in the 0.05% loaded system though is well out of the error bars of both systems so it is reasonably safe to say that the increase in modulus is a true increase.

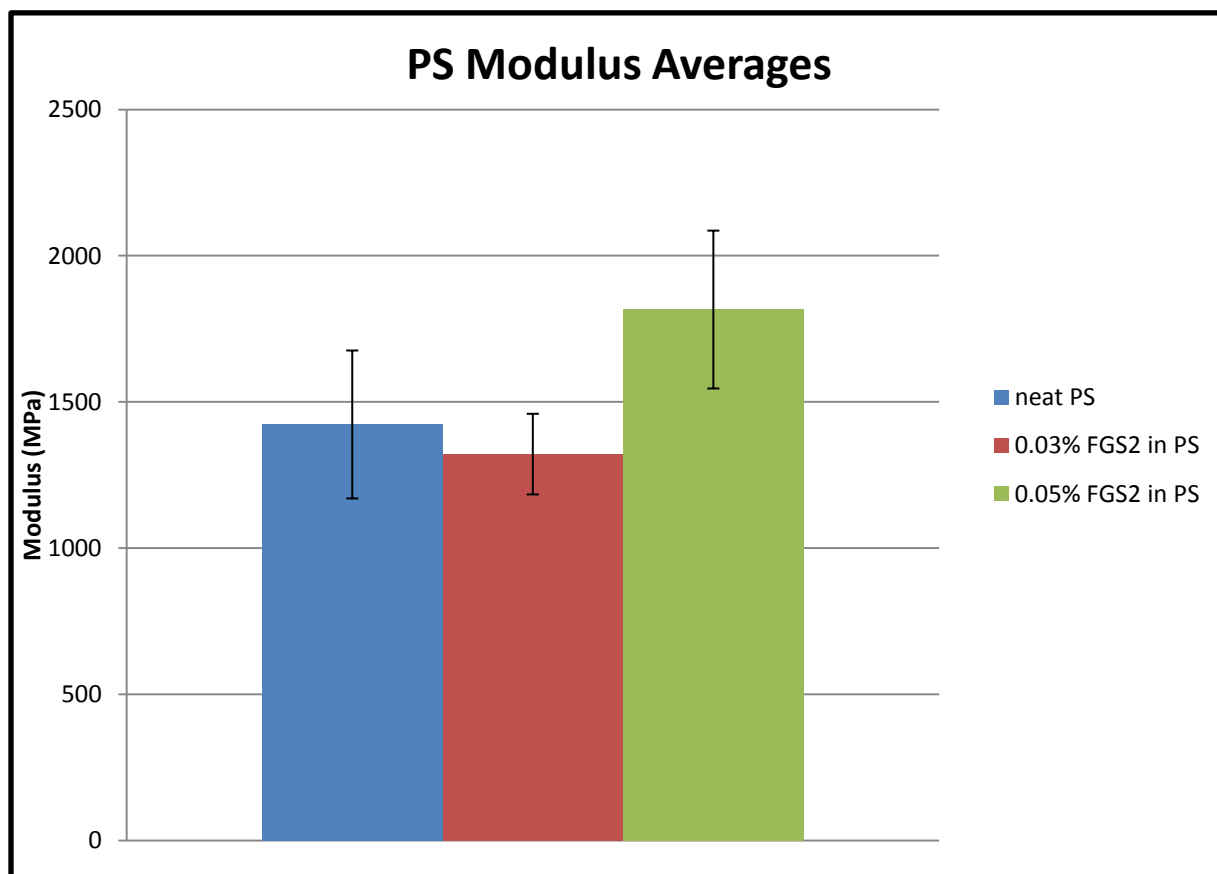


Figure 3 This is a graph of the moduli of the neat PS system, the 0.03%, and the 0.05% loaded GO in PS systems with error bars

It is also important to note that the loadings for the PS system are less than those in the PEI system. This is because a 0.1% loaded PS system was tried several times; however, the GO tended to clump at that high of a loading in PS. Since the GO clumped together, it was impossible to get a true nanocomposite so then it would have been unwise to test it. Without a uniformly dispersed nanocomposite, all of the advantages of the nanocomposite have been lost so it could be likely that any tensile testing will only apply stress to the neat section of polymer. Therefore the results would essentially be useless. There are several reasons for which the GO could have clumped together

however it was decided to move onto a lower loading of 0.03% as opposed to trying to fix the problem because it was determined to be more likely to get a good measurement at the lower loading.¹³

Name	Modulus (MPa)	Elongation at Break (MPa)	Stress at Break (MPa)	
neat PS	1743	0.97	20.34	
neat PS	1433	0.47	8.26	
neat PS	1033	0.40	12.08	
neat PS	1455	0.65	15.36	
neat PS	1452	0.54	10.32	
Averages	1423	0.60	13.27	3.6% Solvent
Std Dev	253	0.22	4.73	
0.03% GO	1276	0.79	13.90	
0.03% GO	1286	0.87	14.26	
0.03% GO	1166	0.96	18.49	
0.03% GO	1520	1.52	27.61	
0.03% GO	1166	1.26	22.74	
0.03% GO	1460	1.75	28.13	
0.03% GO	1379	2.33	34.08	
Averages	1322	1.35	22.74	3.9% Solvent
Std Dev	138	0.56	7.63	
0.05% GO	2056	0.76	20.50	
0.05% GO	1905	1.41	33.71	
0.05% GO	1531	1.38	21.28	
0.05% GO	1948	1.14	25.55	
0.05% GO	2034	1.65	34.09	
0.05% GO	1425	1.29	20.67	
Averages	1816	1.27	25.97	3.6% Solvent
Std Dev	270	0.30	6.42	

Table 2 Shows the modulus, elongation and stress at break for the three PEI systems along with solvent content

Looking more closely at the 0.03% GO loaded system, some odd things jump out of the page.

Both the stress and strain at break have increased for the system, but the modulus of the system dropped. This would be because the stress at break did not increase at the same rate as the strain at break. Now the reason for the increase in stress and strain is likely due to the interactions between the GO and the PS where as the slight drop could be from the increased solvent content. The interaction between the PS and the GO is most likely the cause for the increase in strain at break where as the stiff

GO is the cause of the increase of stress at break. It is possible that there is a weak interaction between the GO and the PS such that there would be slipping between the PS and the GO sheets. This should allow the nanocomposite to stretch further giving a higher strain at break.¹⁴ Though there is slipping between the sheets and the PS, there must also be some attraction between the two as there is also an increase of almost 2 times in the stress at break between the loaded and neat system. The reason for the decrease in modulus may however be attributed to the change in solvent content. There is a small difference in solvent content between the other two systems and the 0.03% loaded system. It has been seen that though there usually a decrease of modulus as the solvent content goes up which is exactly what happens in this case. Thus it makes sense that the 0.03% loaded system would have a slightly lower modulus than the neat system.

The 0.05% GO loaded system is more easily compared to the neat system as the solvent content for both systems are exactly the same. With solvent content not a problem, it is easy to see the positive effect the GO has had on PS. All of the major properties of the system increase with the addition of GO. The stress and strain at break both increase as well as the modulus. The effects look similar to that of the 0.03% loaded system, but the higher solvent content seems to have a positive effect. The increase in the modulus is very large in comparison to both the error bars and the PEI systems. The 0.05% loaded PEI system only saw an increase in modulus of around 25 MPa where as the 0.05% loaded PS system saw an increase in modulus of around 400 MPa.

Conclusion

In the attempt to create new materials with better properties, successful attempts were made with both PEI and Polystyrene. Both materials showed an increase in the modulus which is the measure of success for the materials. It was also important to set up a successful method for the development and casting of the solvent made films though it is possible that a new polymer system will require some

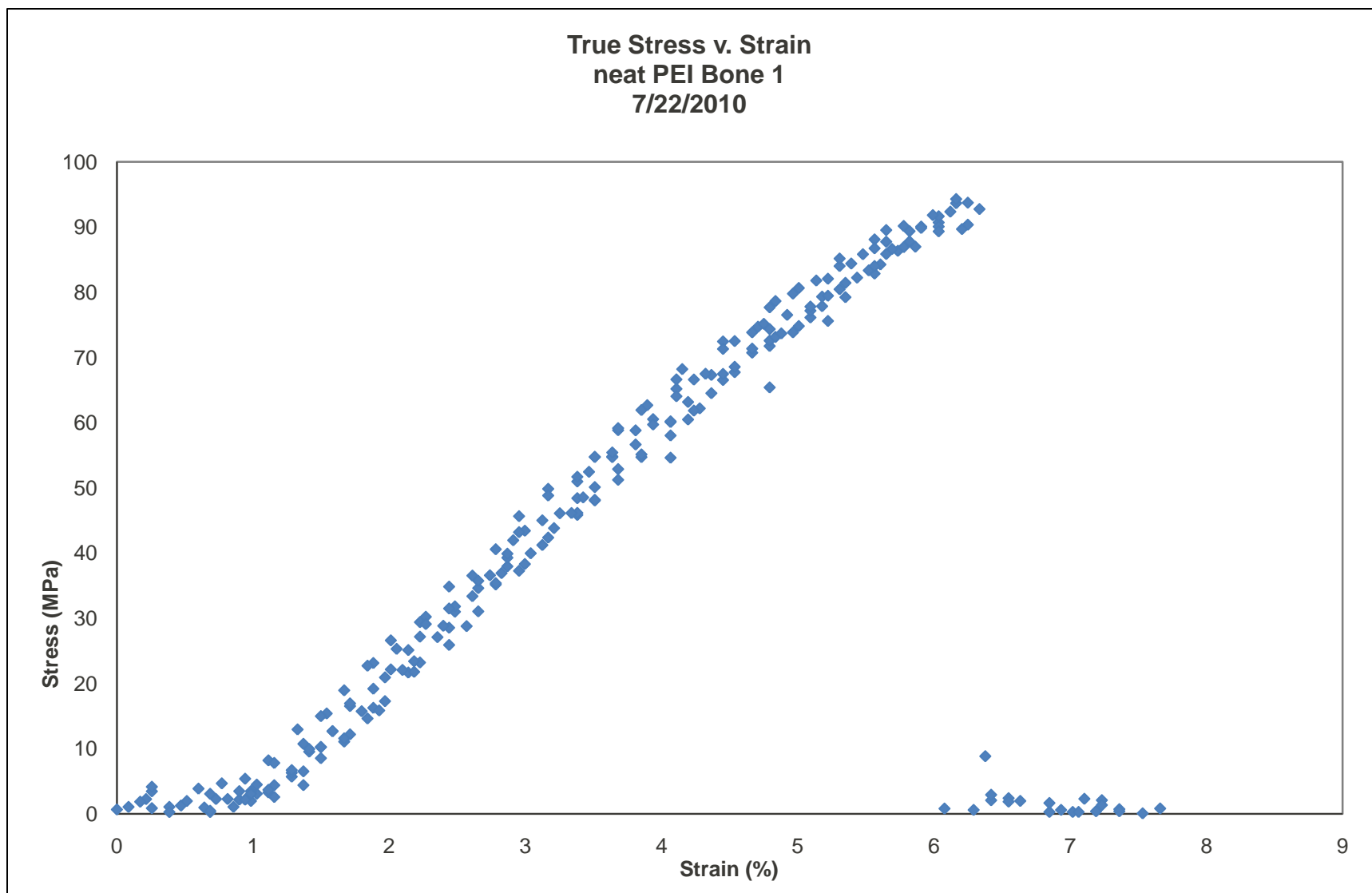
new techniques in order to get an evenly dispersed film that has a limited solvent content and little water. Hopefully other polymer systems can be tested that will show a higher degree of modulus increase due to a higher interfacial adhesion between the GO sheets and the polymer. It has been reported that the interfacial adhesion of both PEI and Polystyrene with GO is weaker than GO and HOPG (highly ordered pure graphene). This shows that there is a lot of possibility to create even stronger materials with different polymers.

There are other areas of research that could branch out of this research. There is the possibility of many other experiments that could be done on the materials. The materials do not have to be limited to only tensile testing. There could be compression testing done on the materials as well as rheological testing which could yield some new and interesting results. Other properties of the material could be tested other than just the simple mechanical features of the materials. These could be things such as gas permeability of the material for the possible use in balloons or possibly some of the optical or electrical properties could be tested. The possibilities are endless for these materials, and the options should not be limited by the creativity of the people coming up with the experiments.

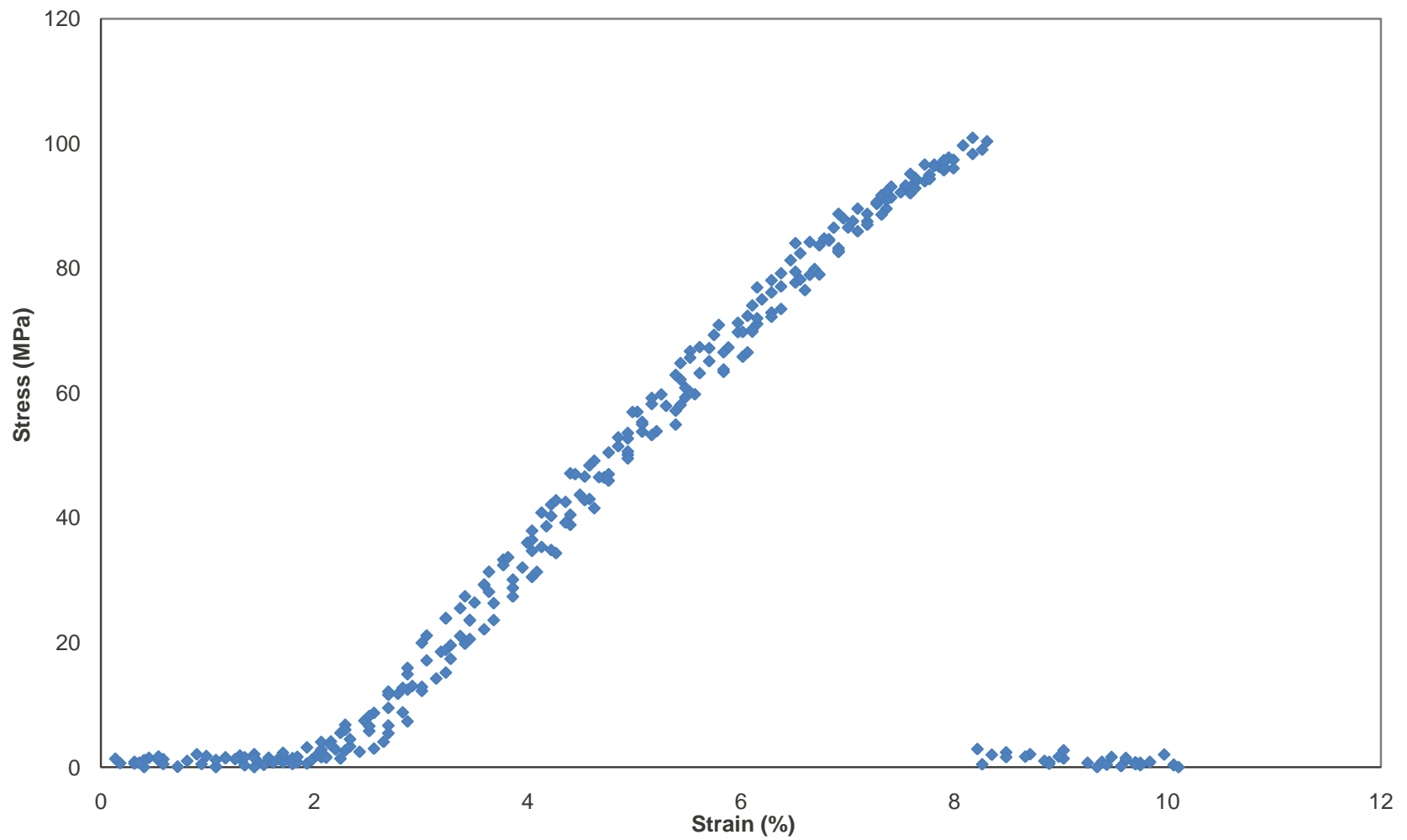
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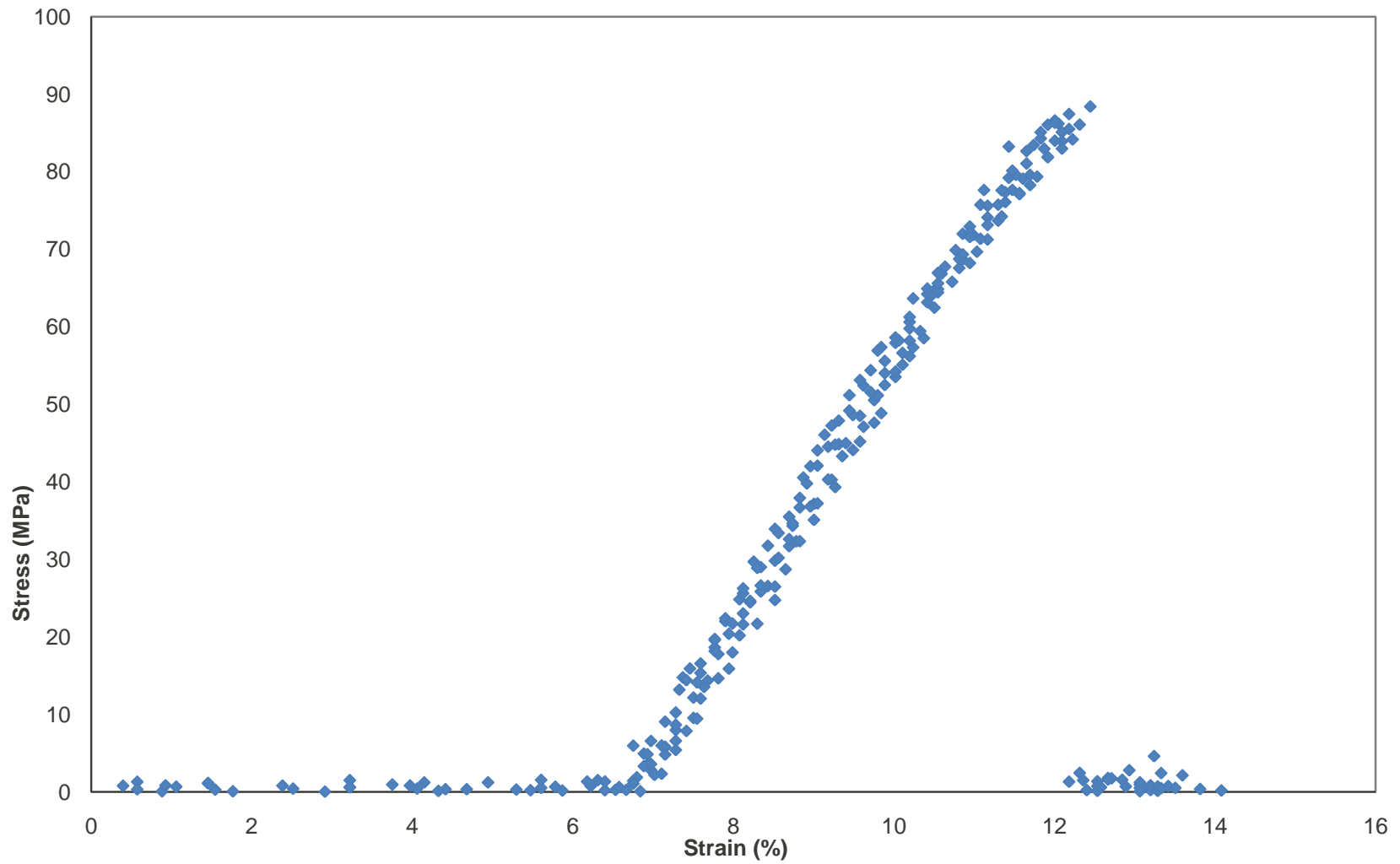
Appendix



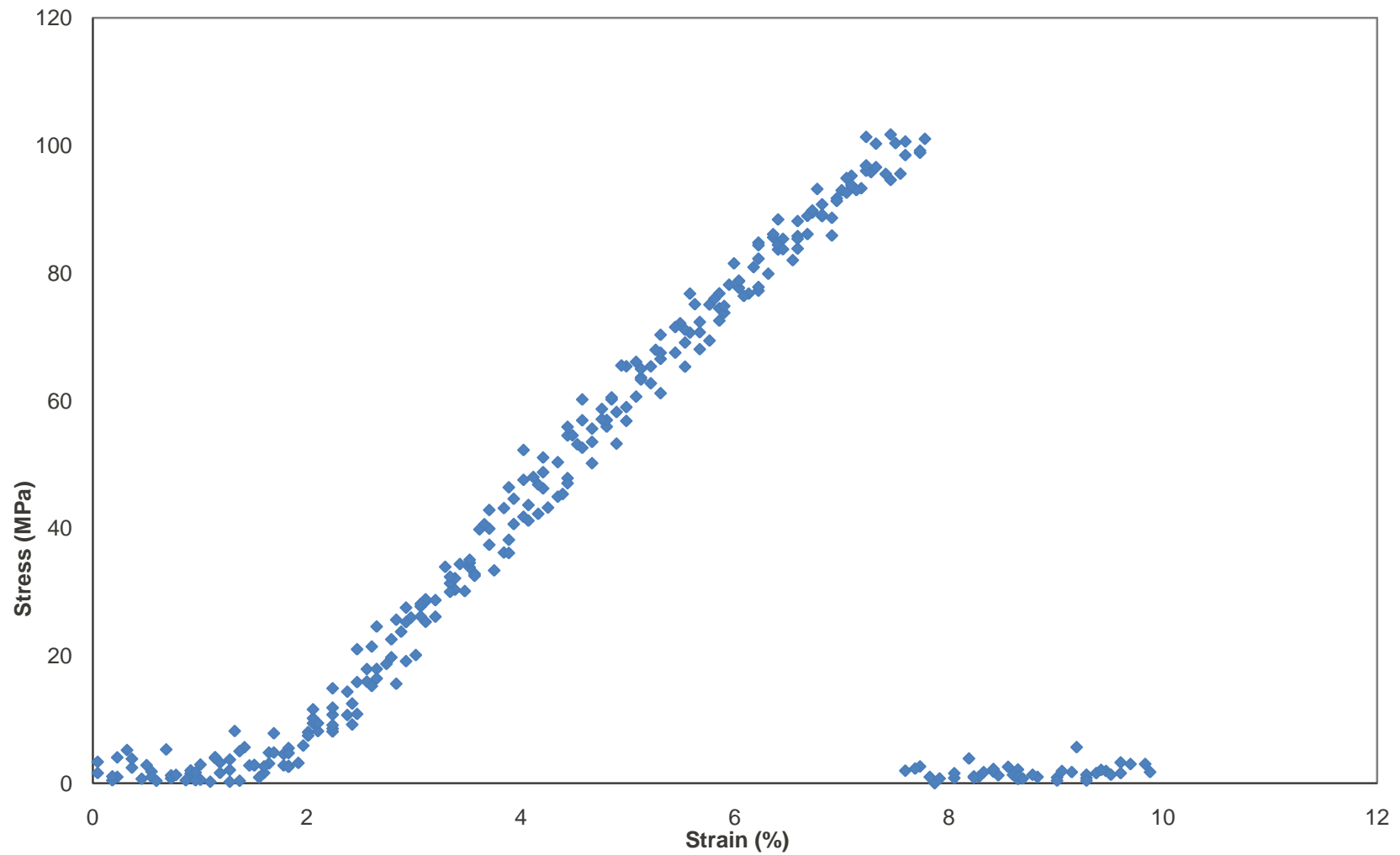
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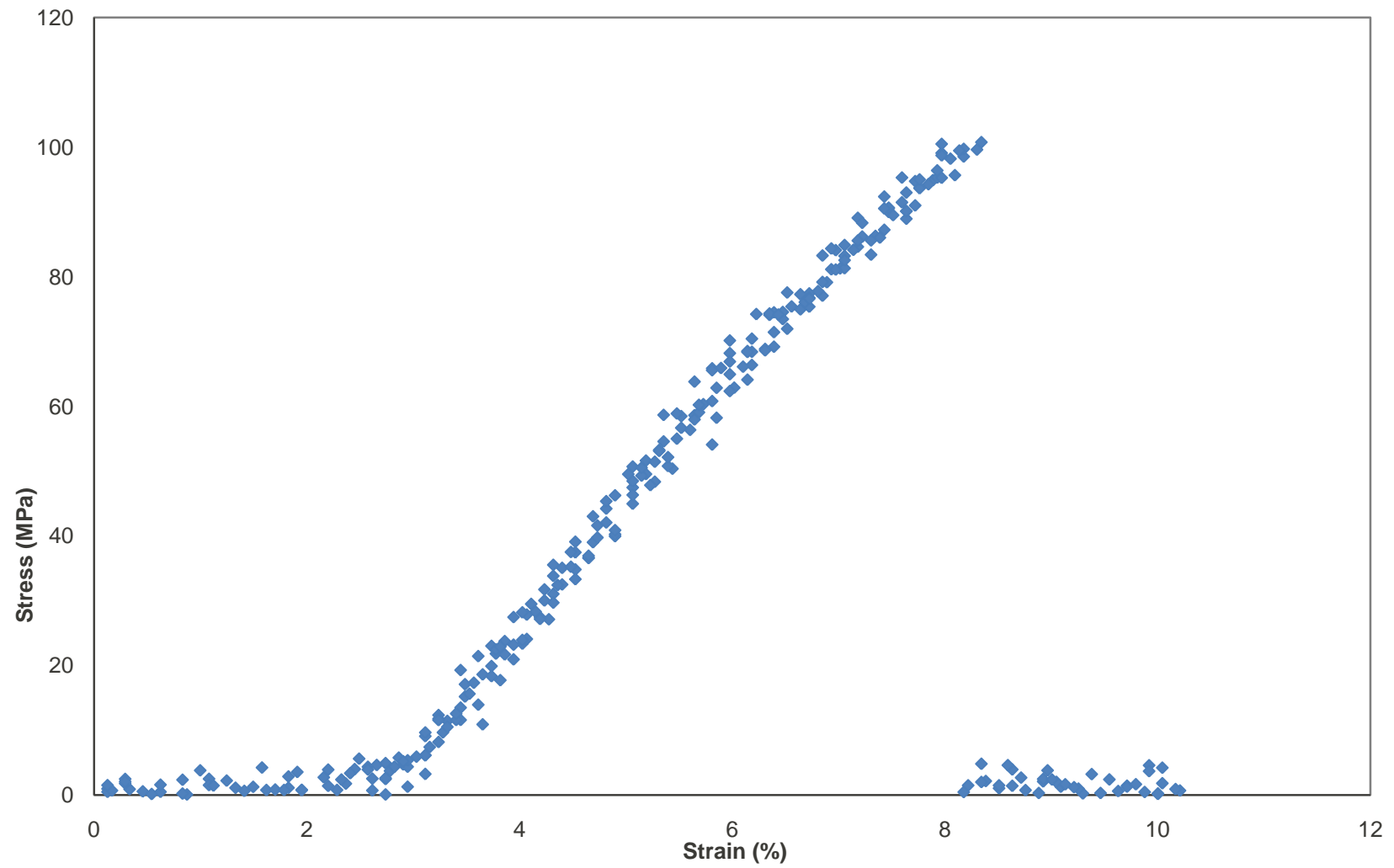
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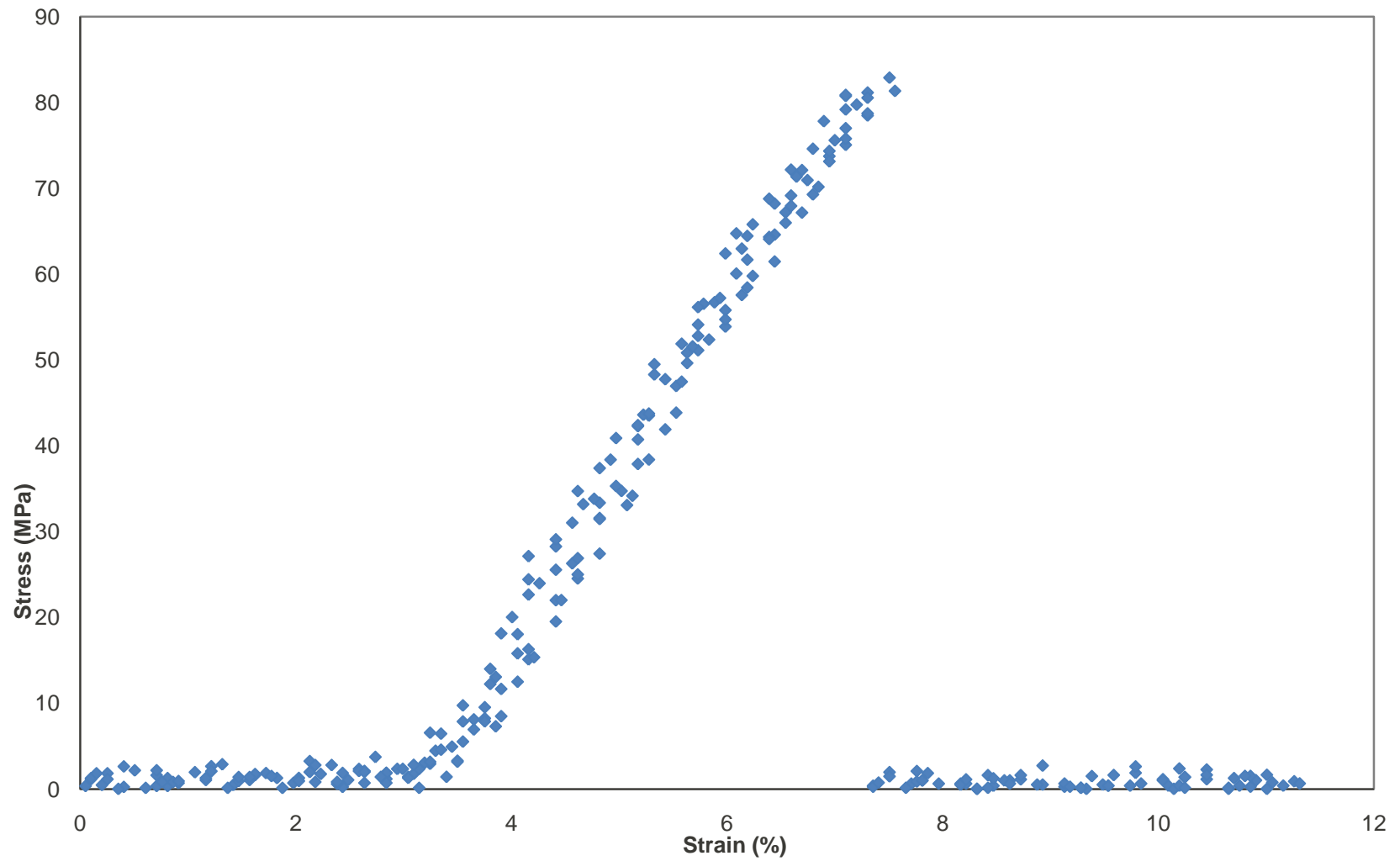
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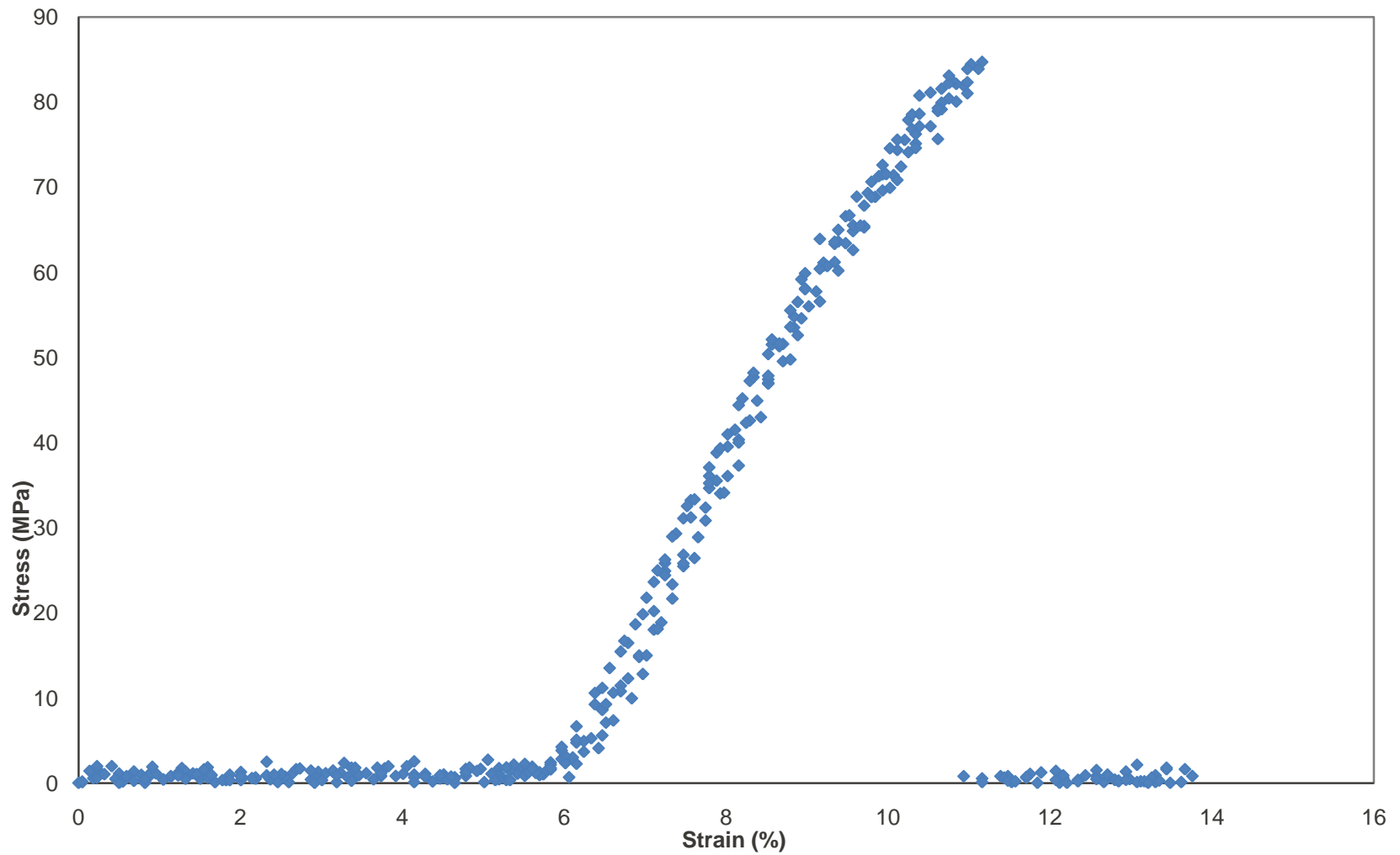
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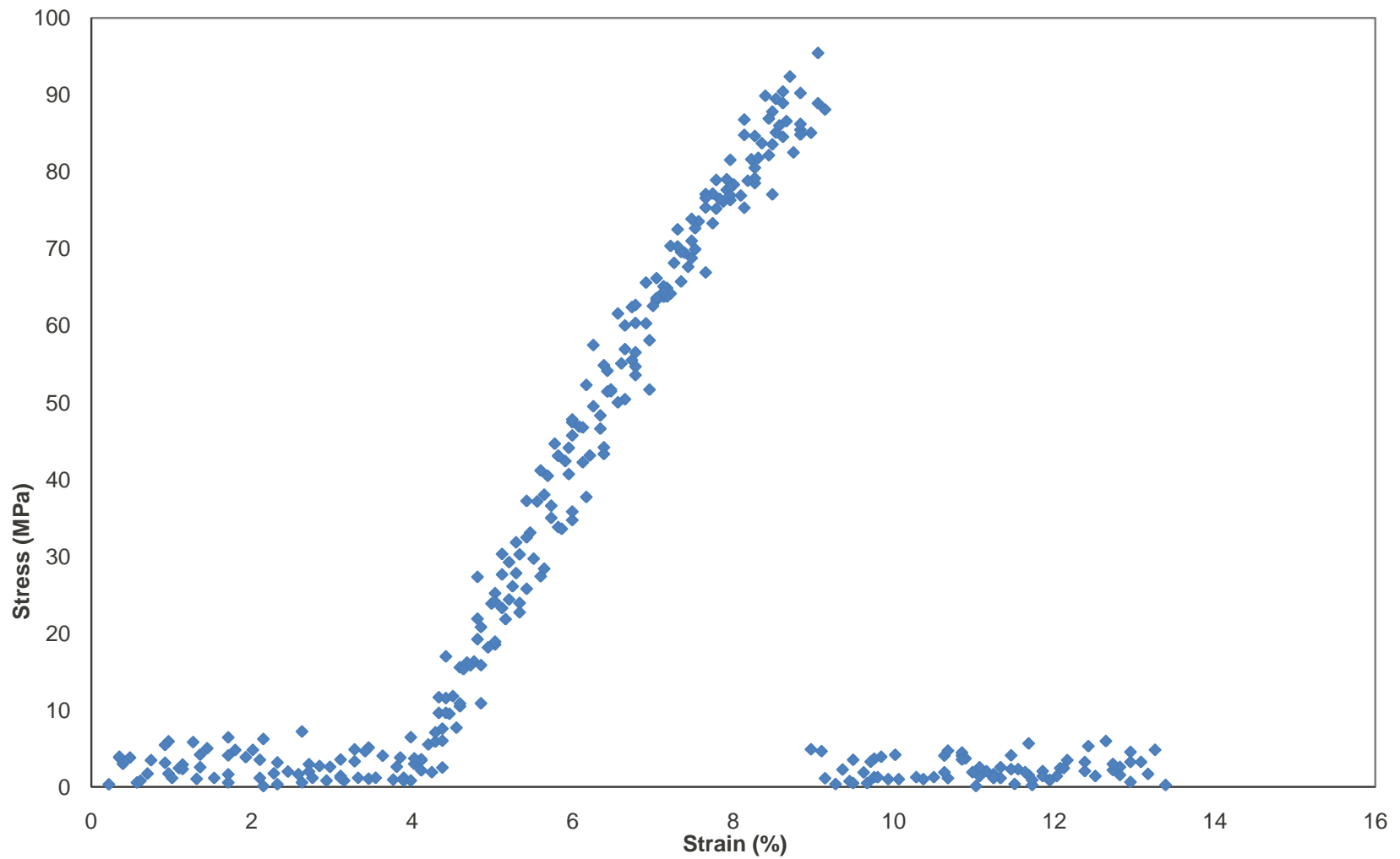
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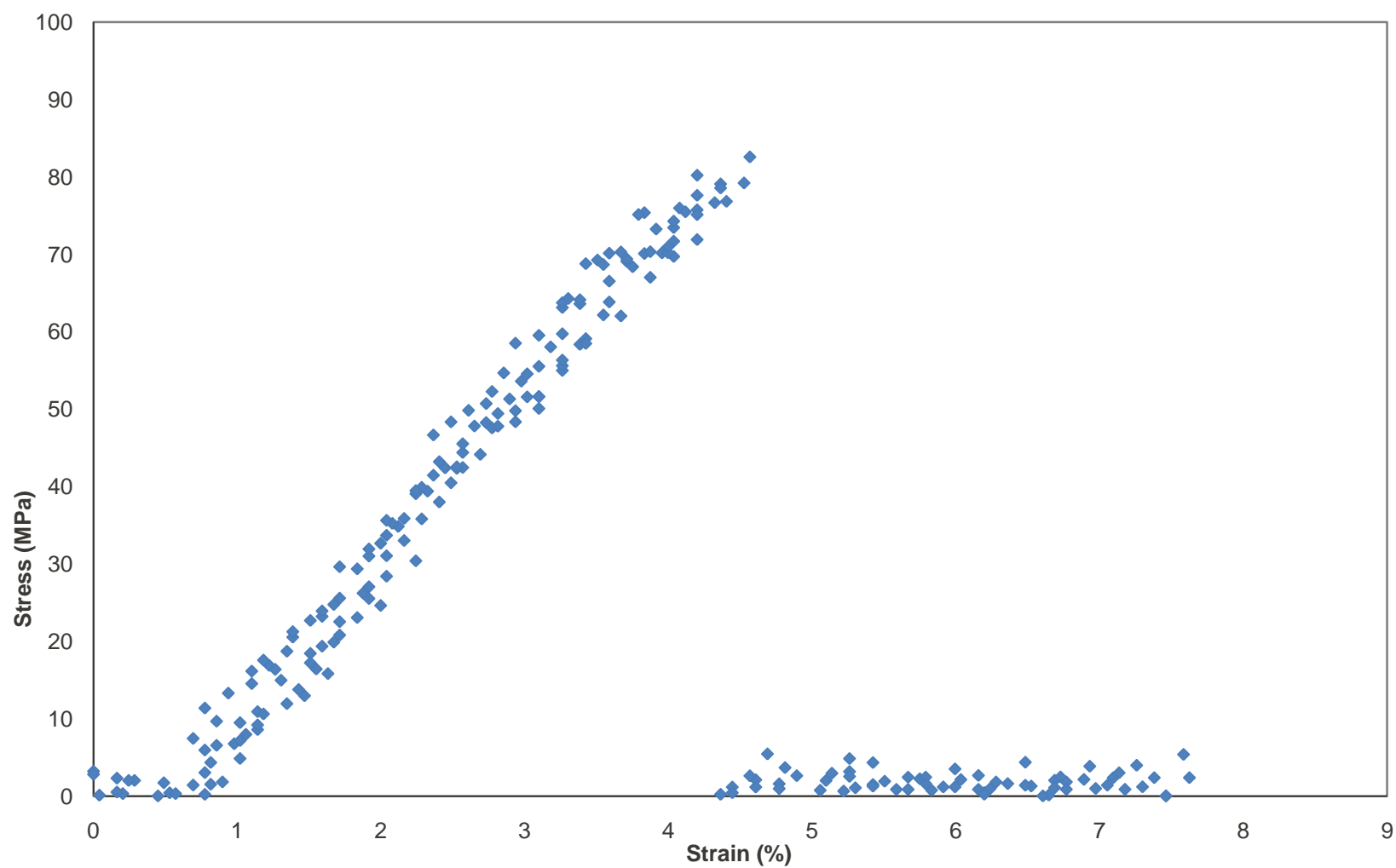
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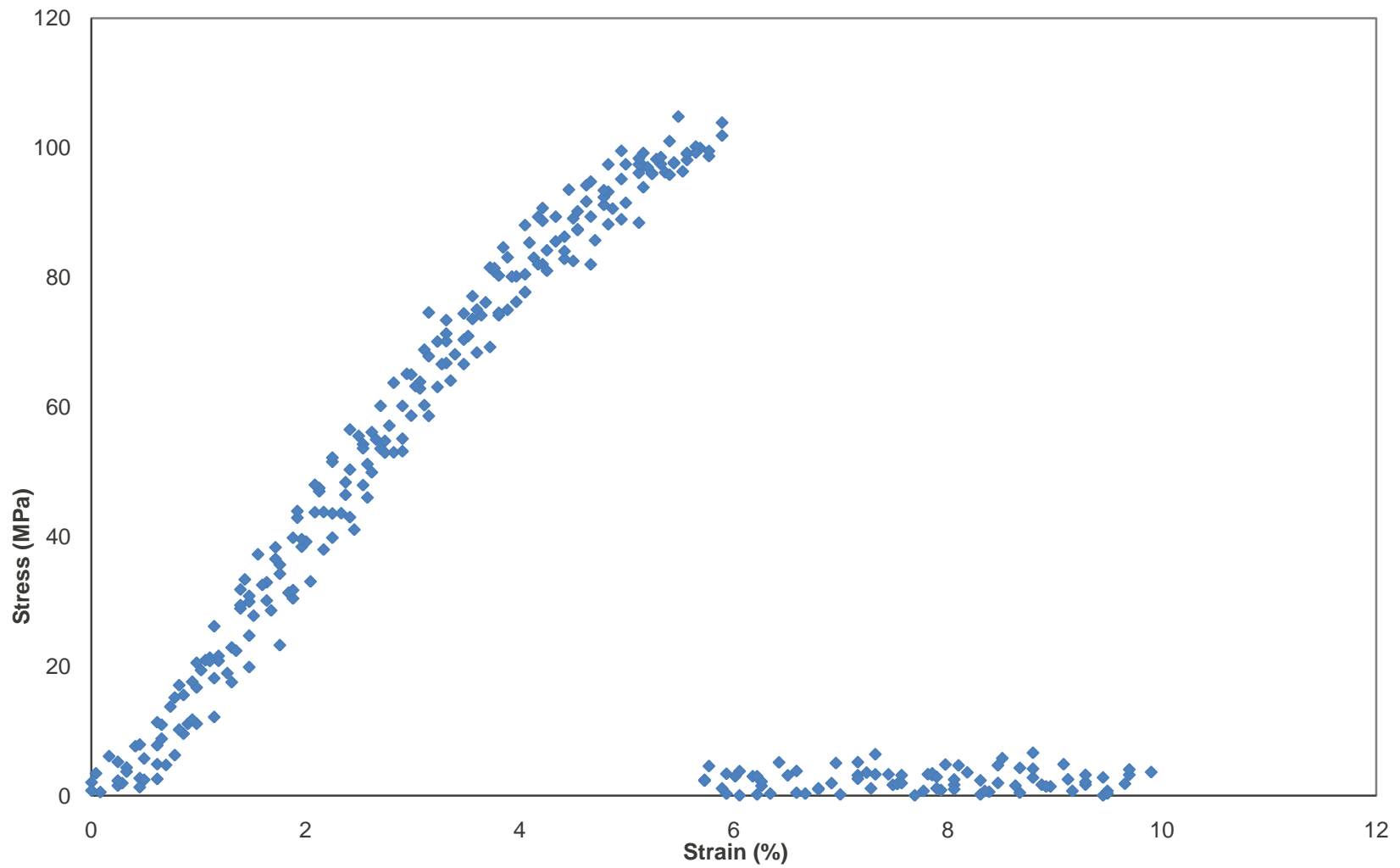
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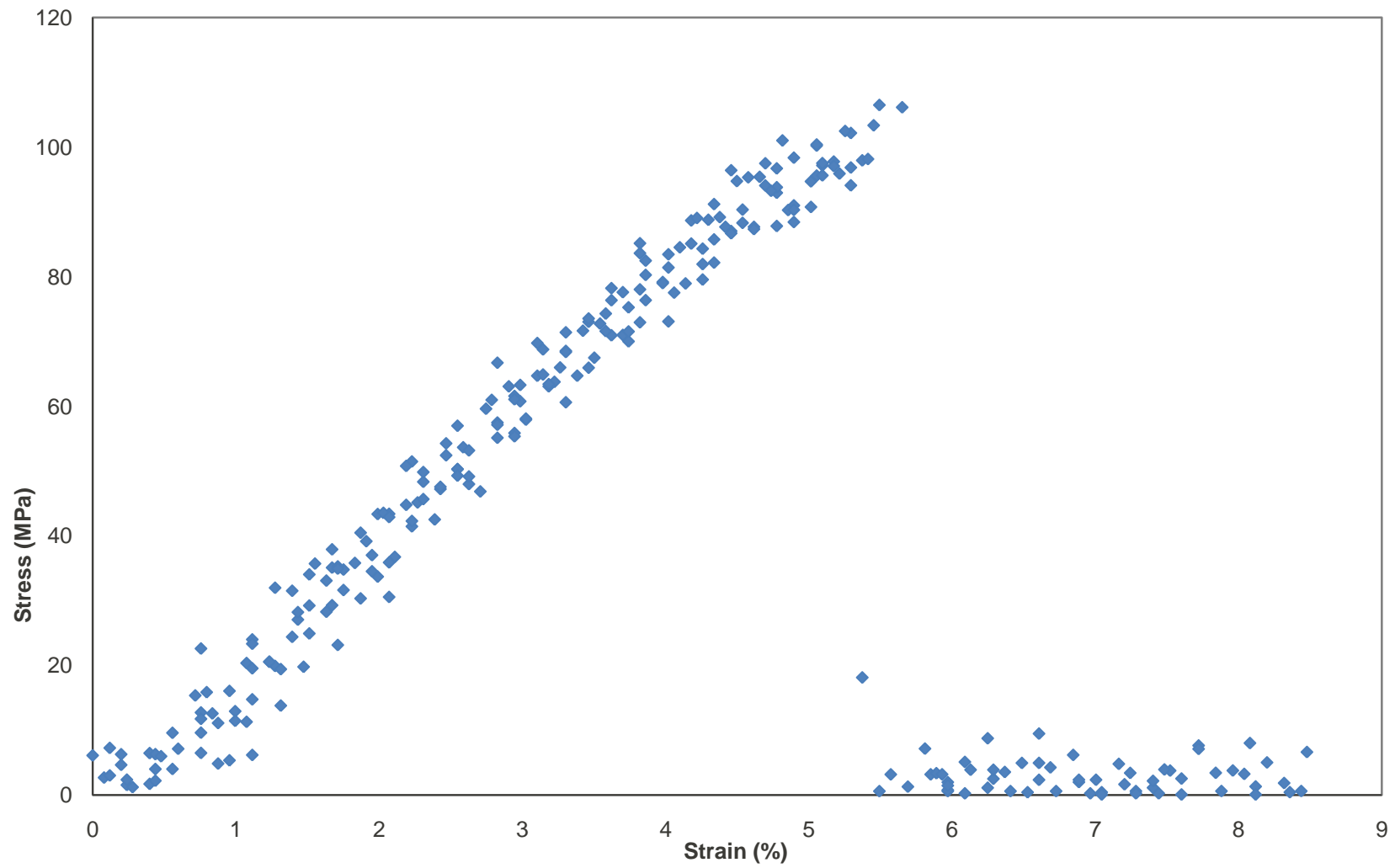
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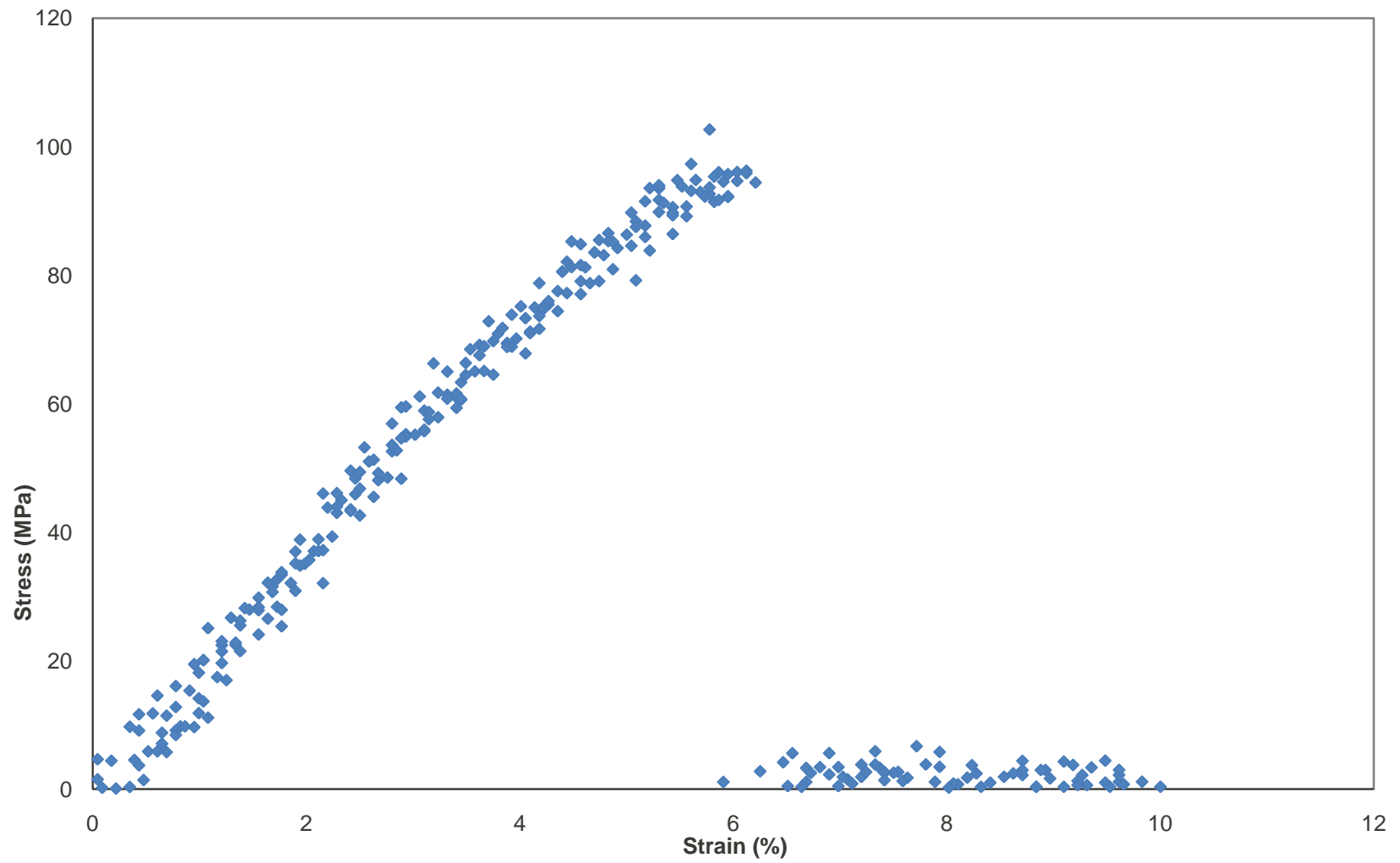
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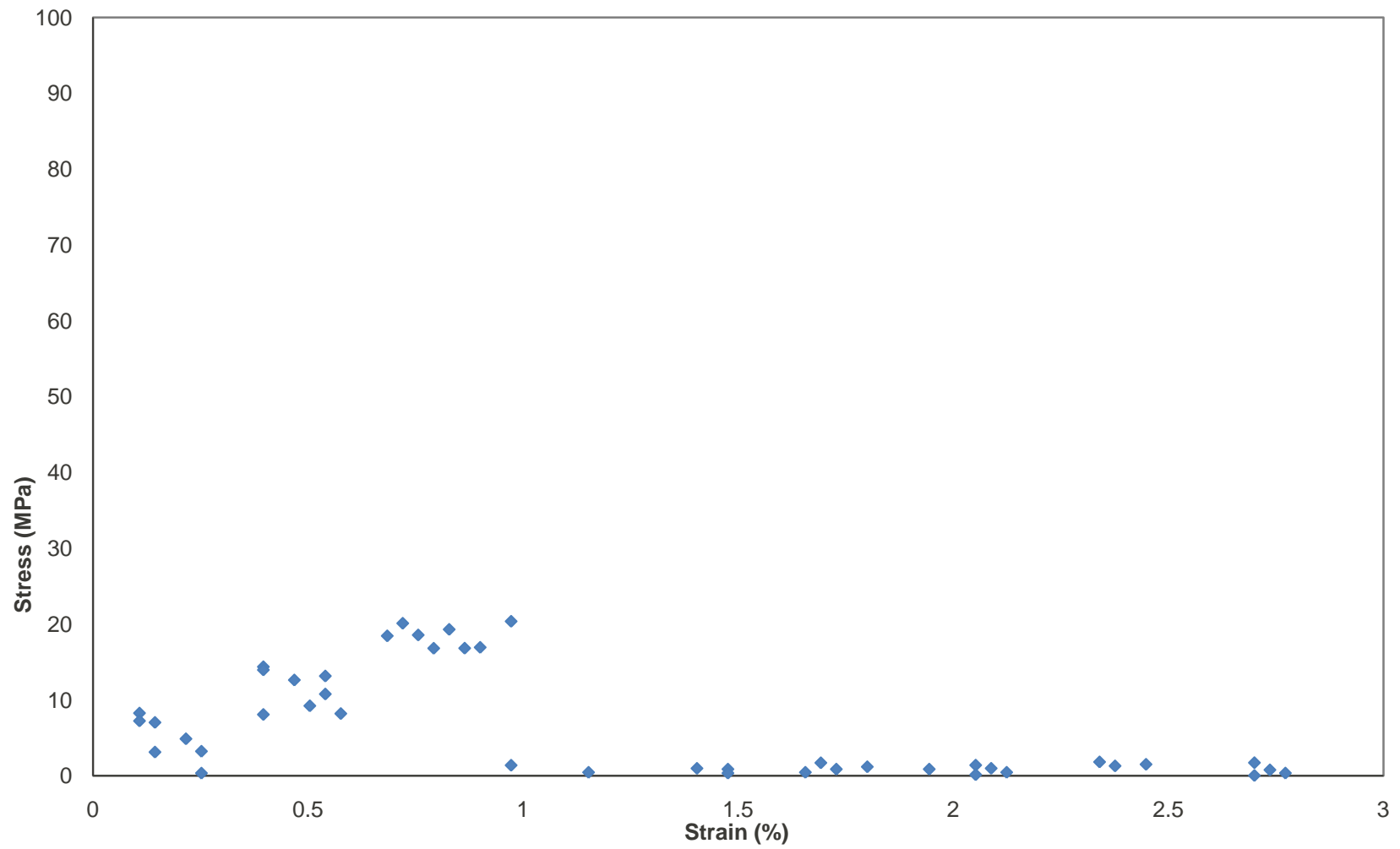
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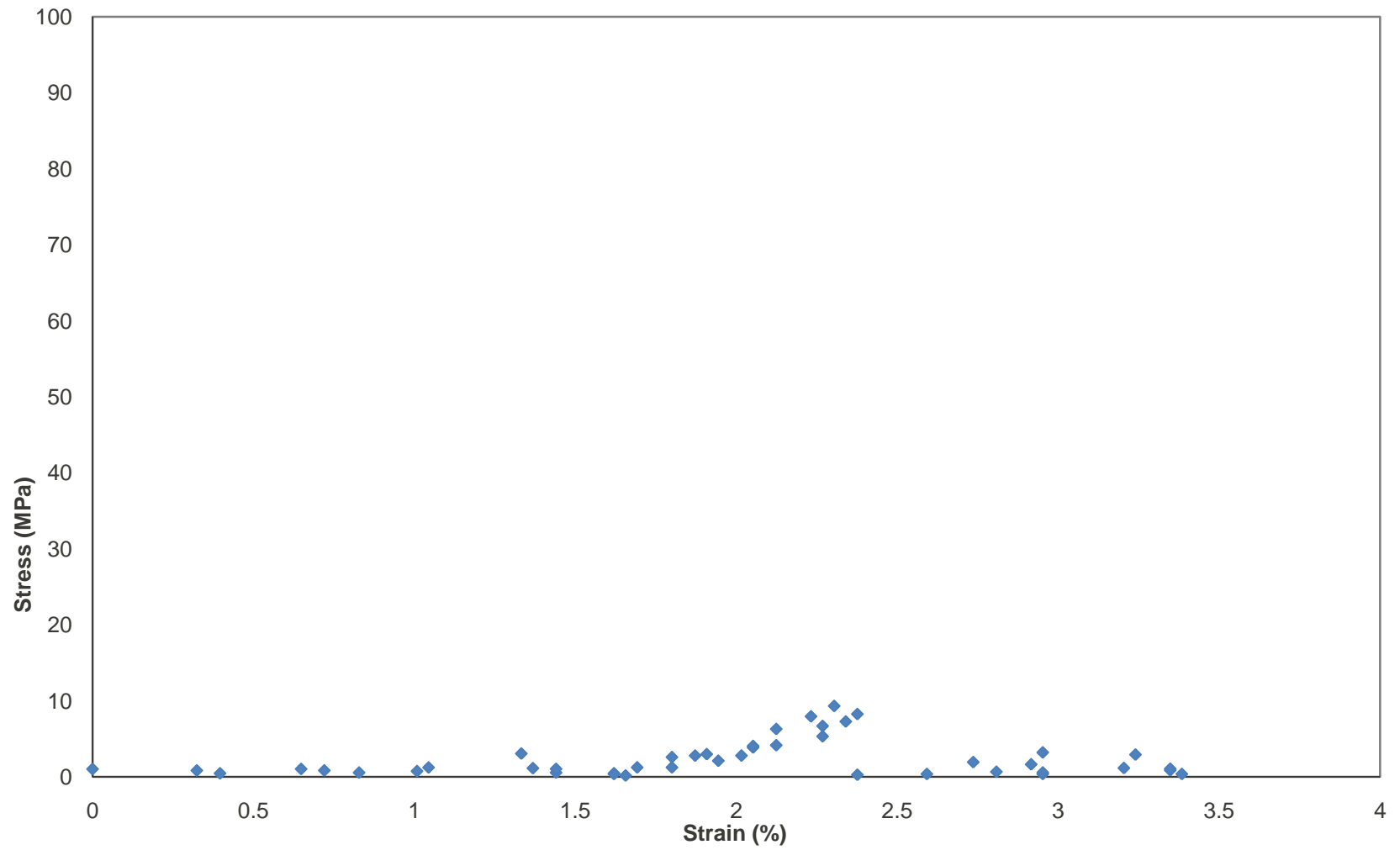
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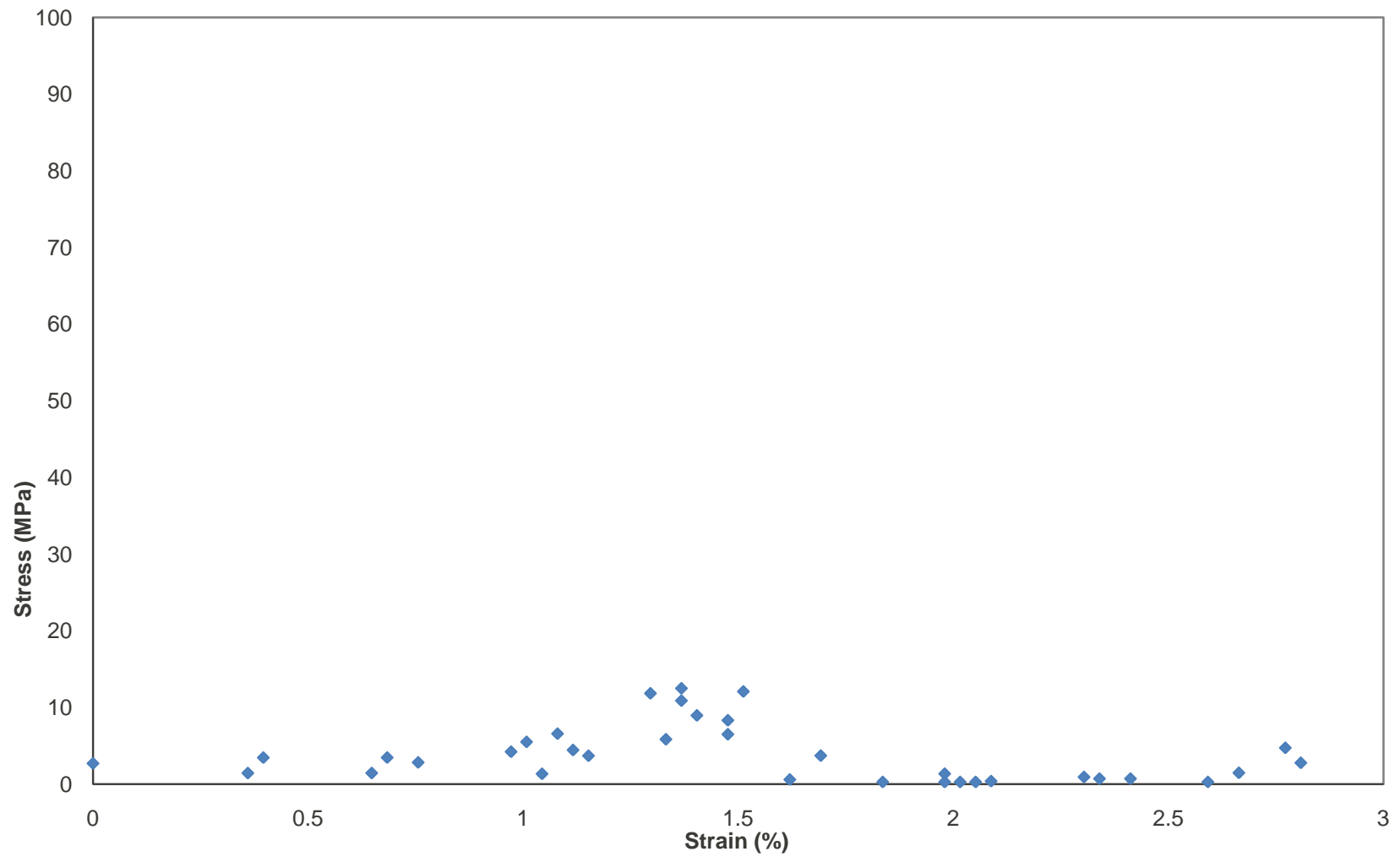
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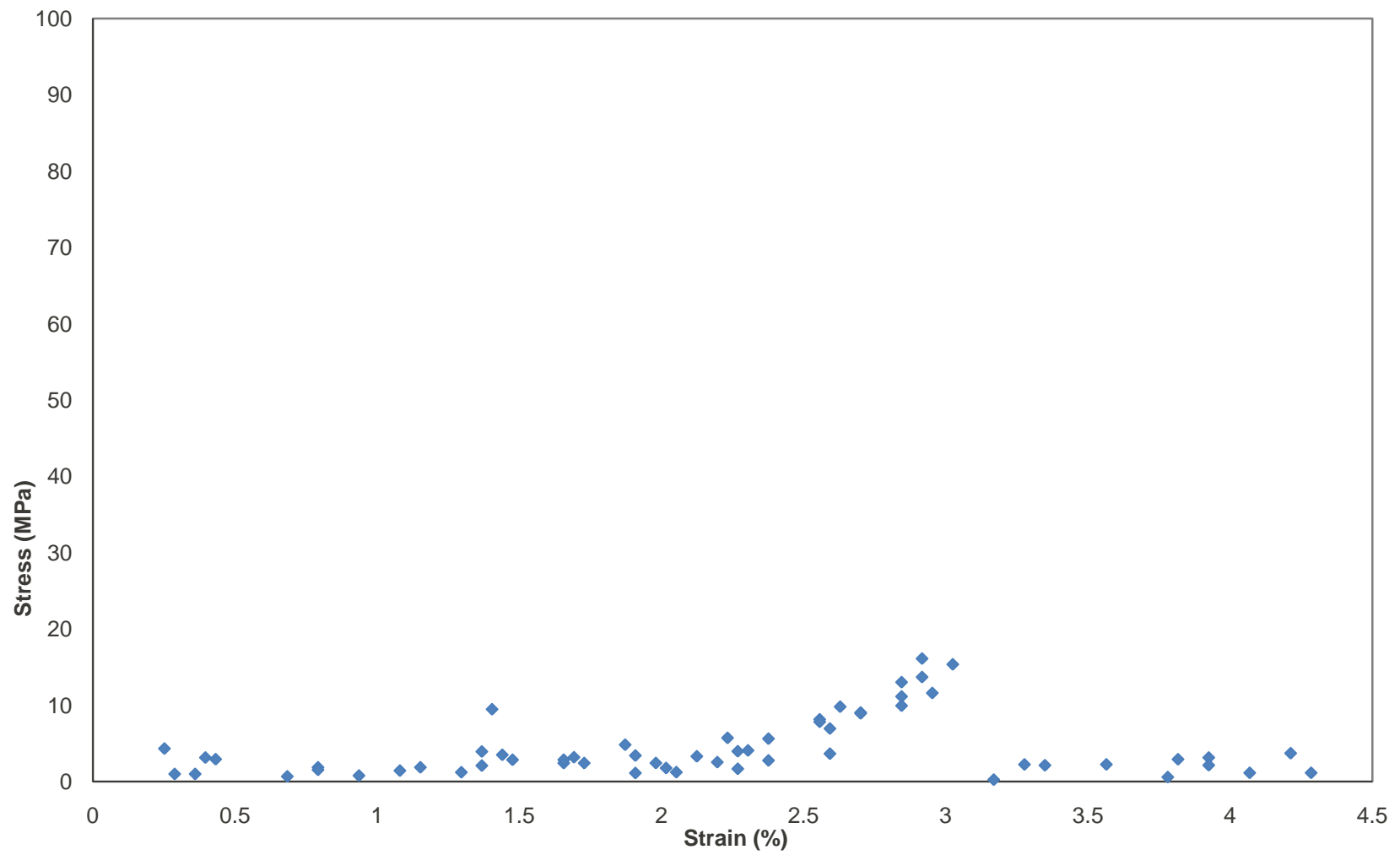
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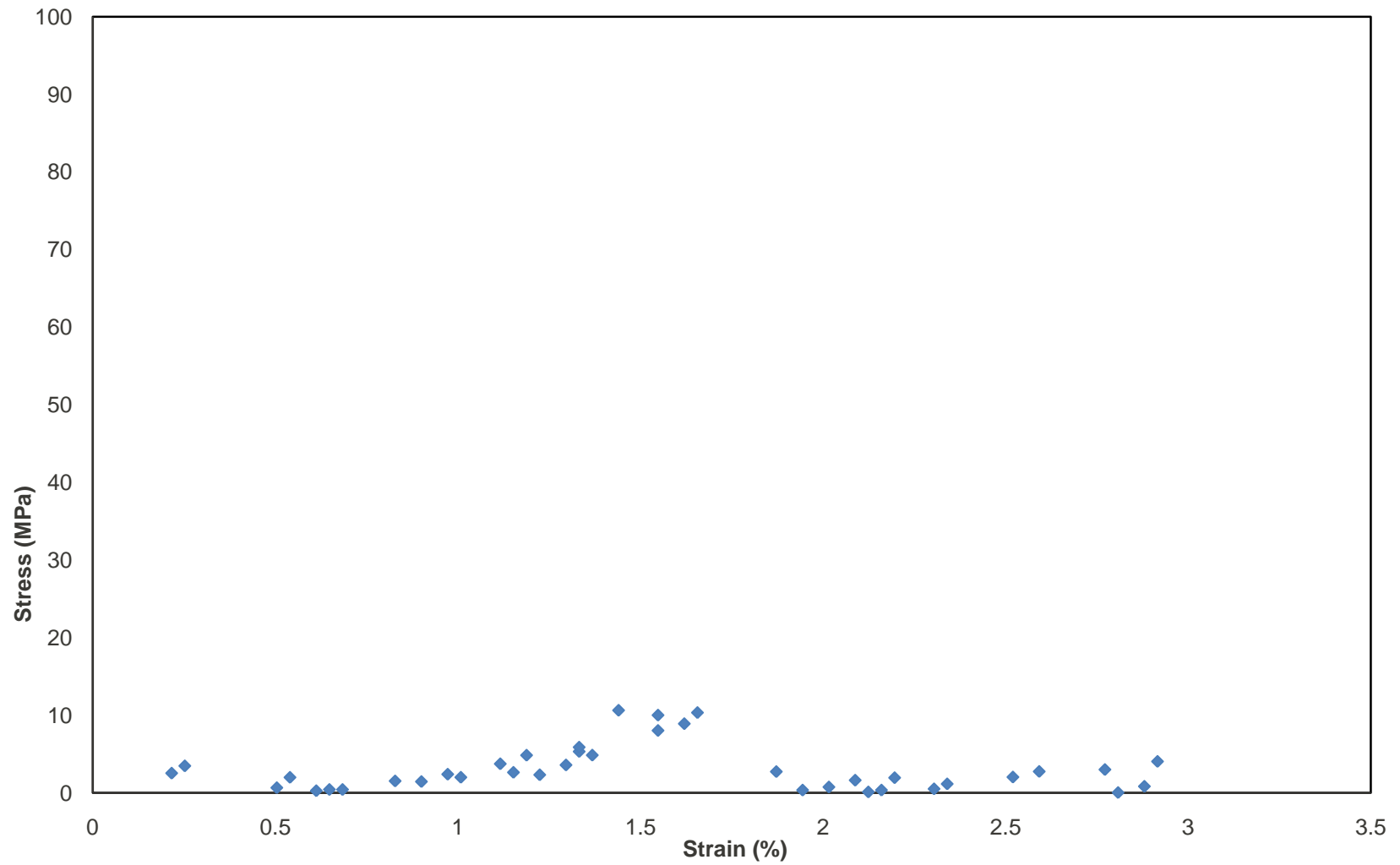
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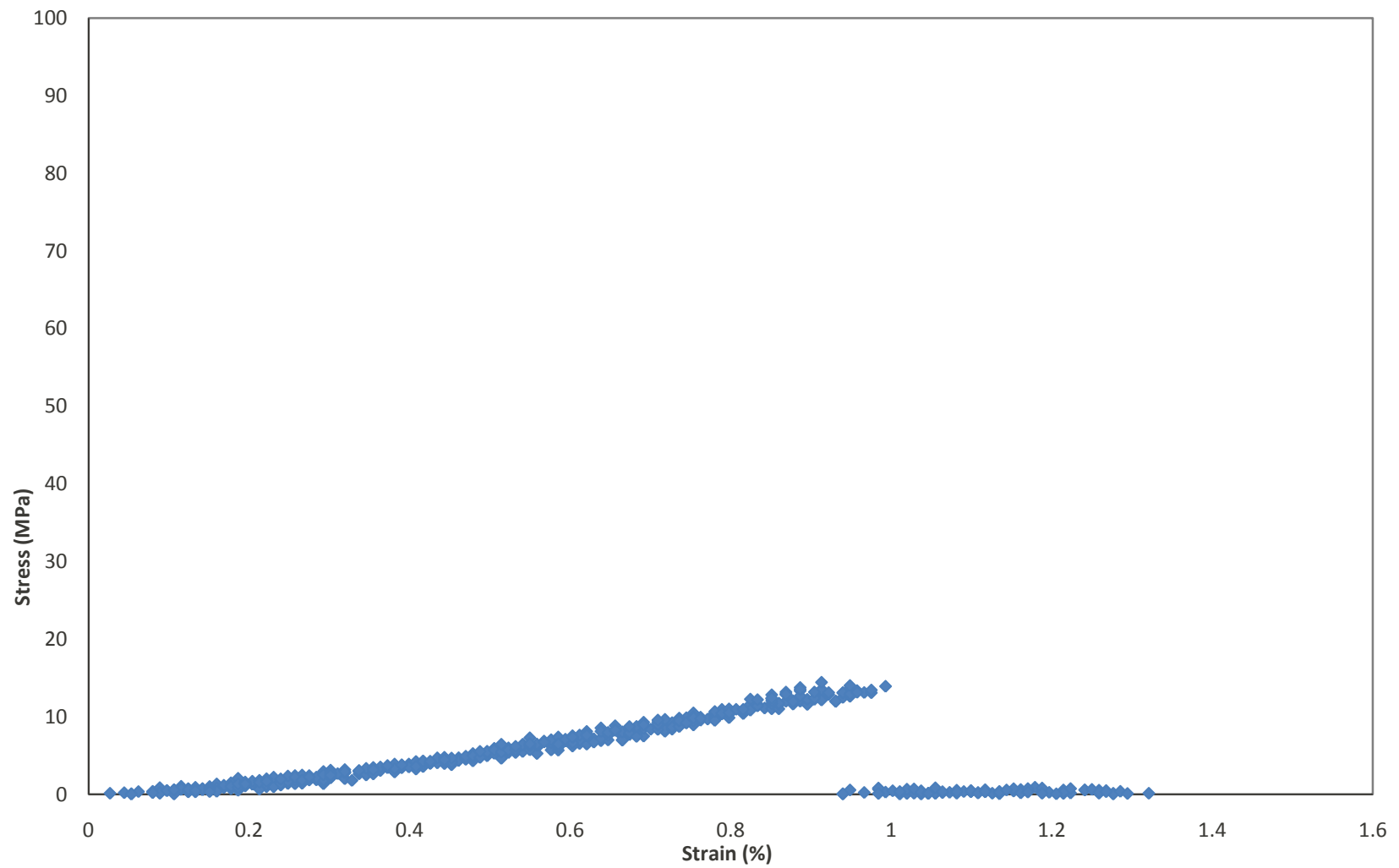
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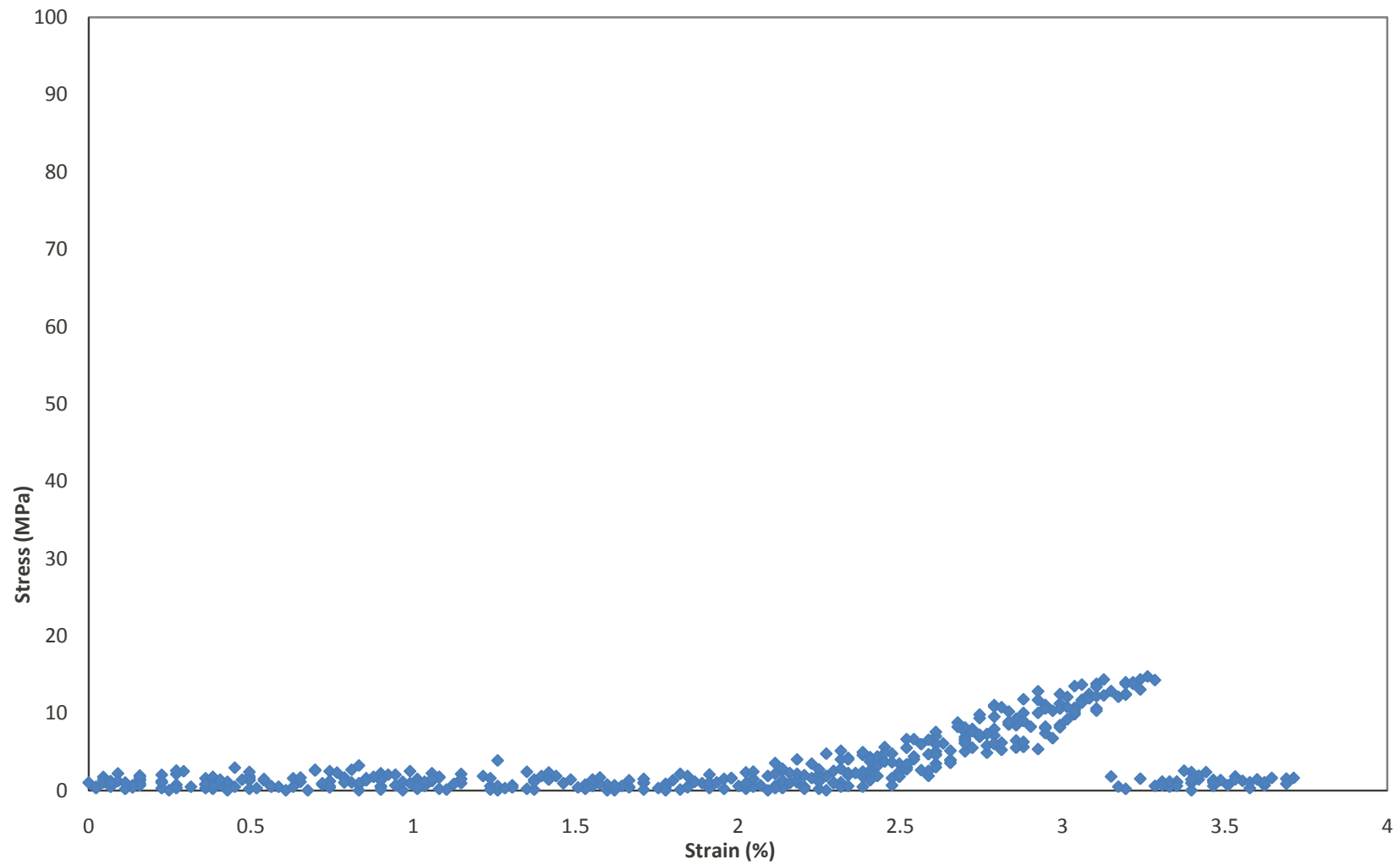
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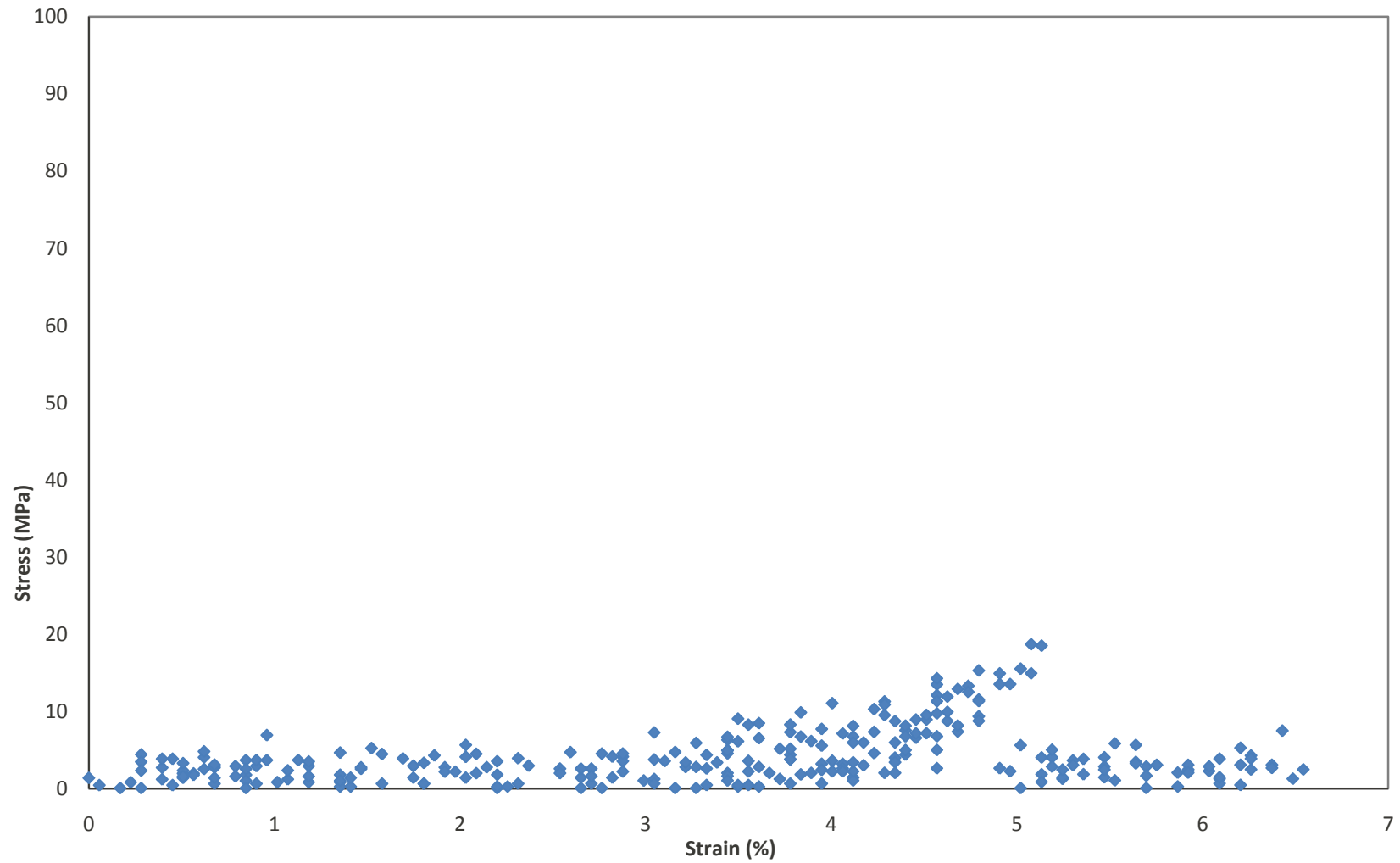
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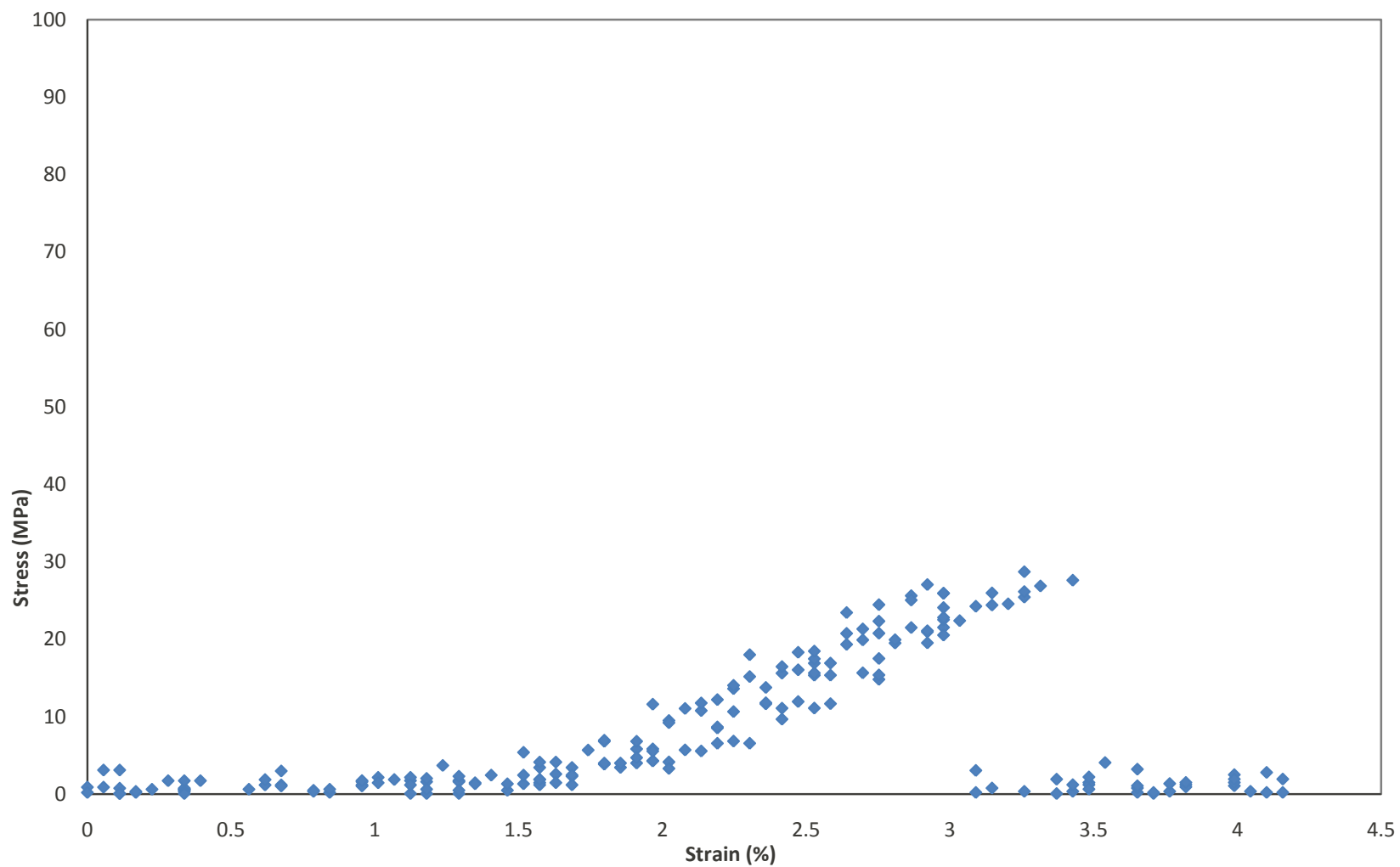
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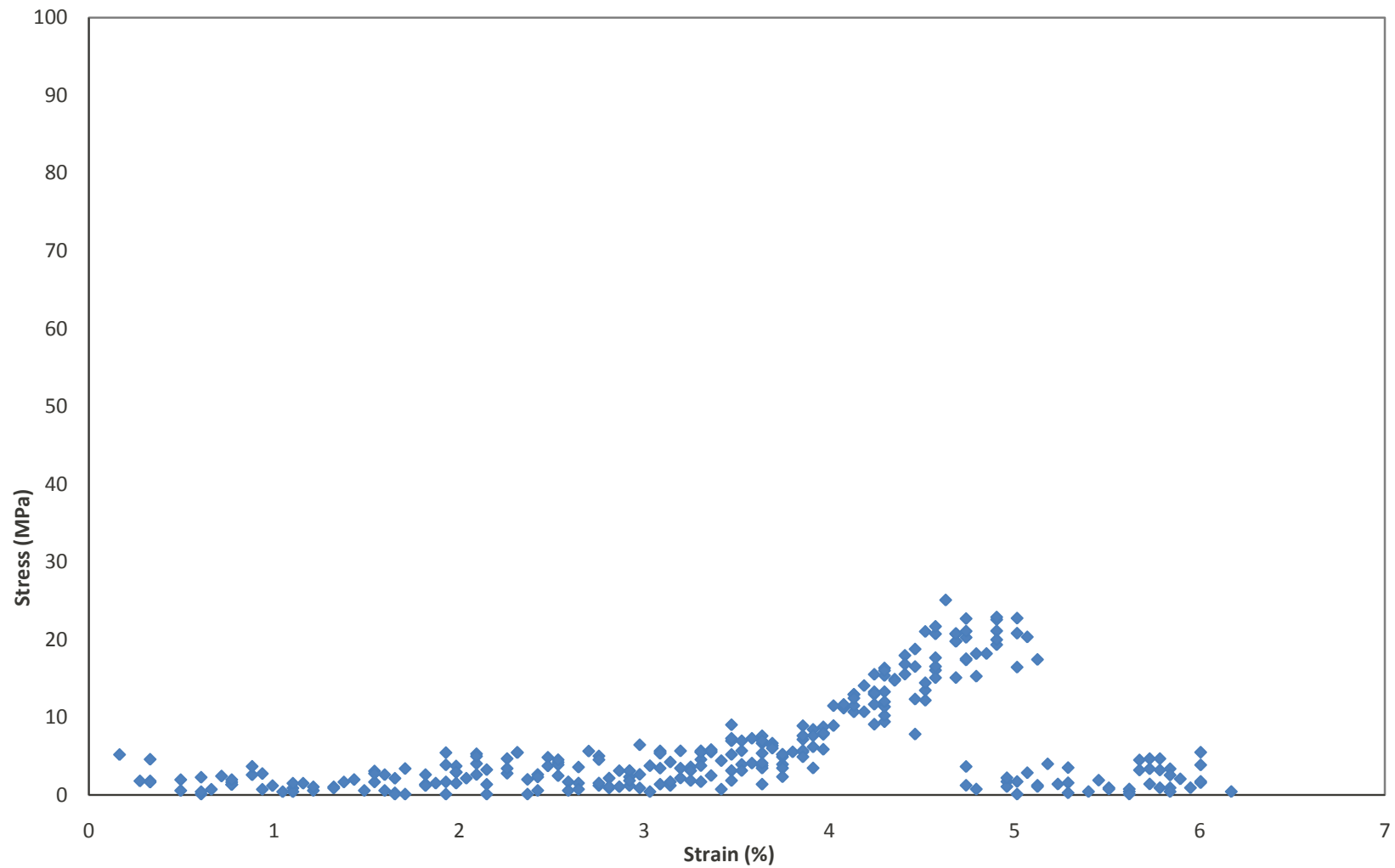
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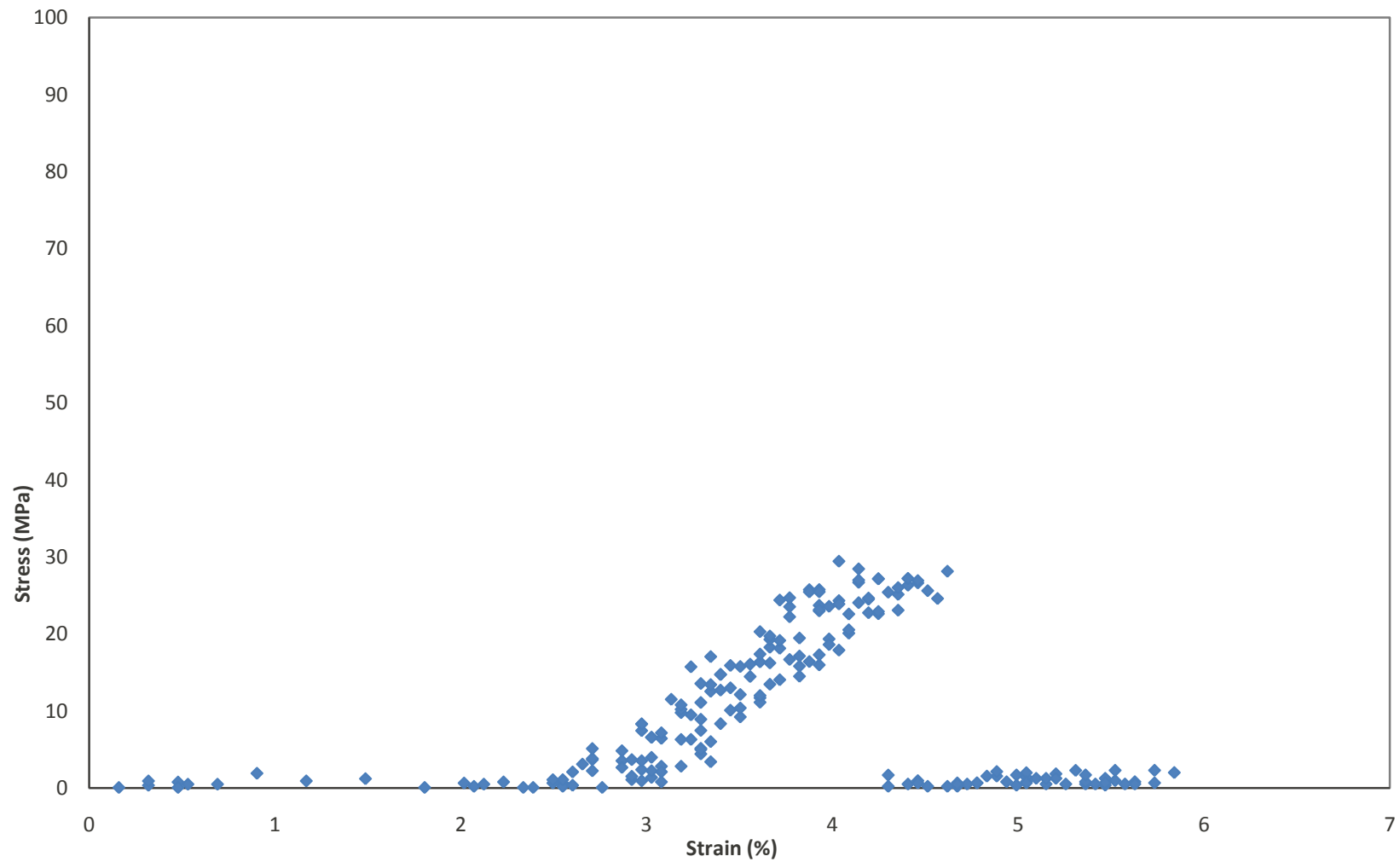
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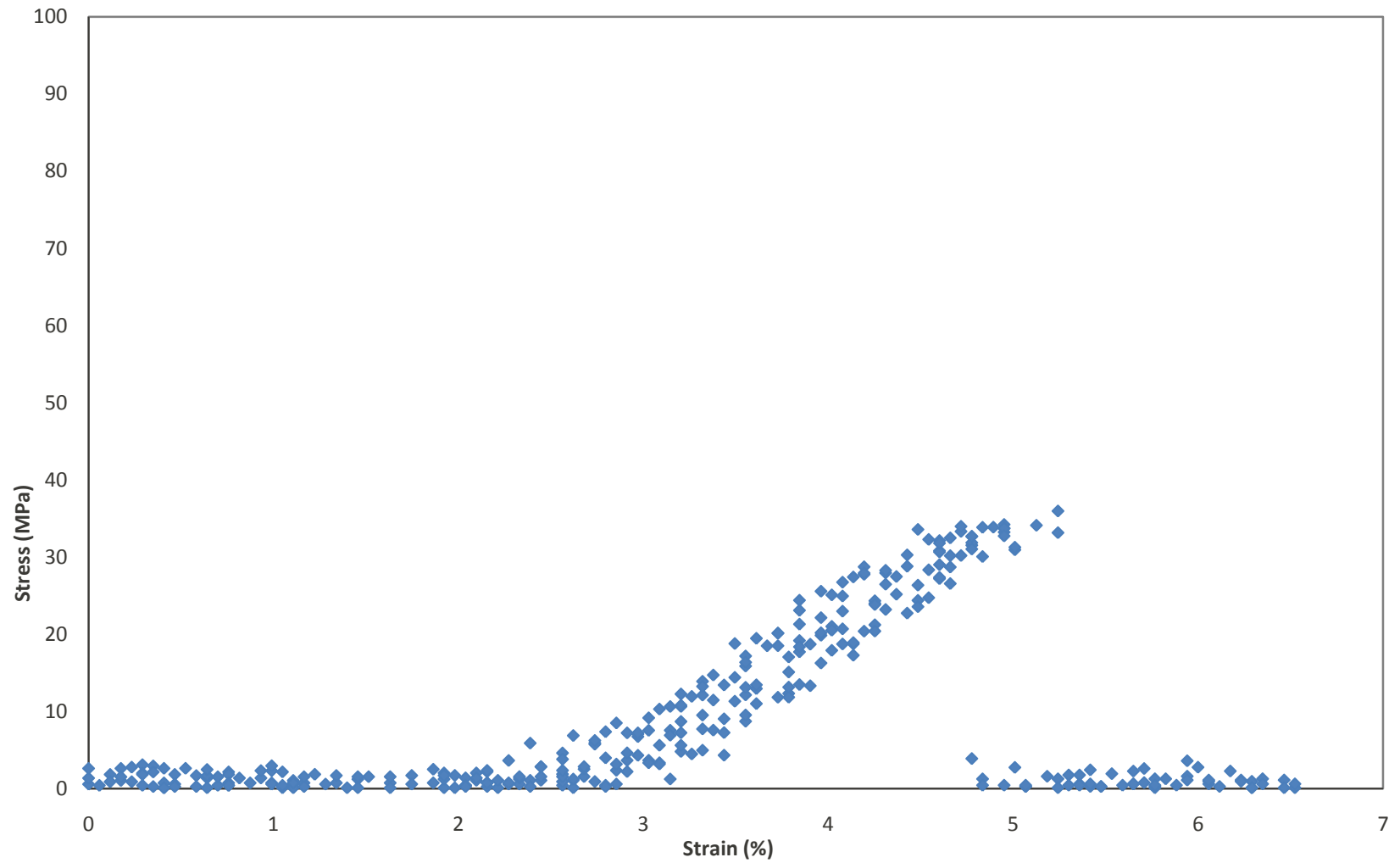
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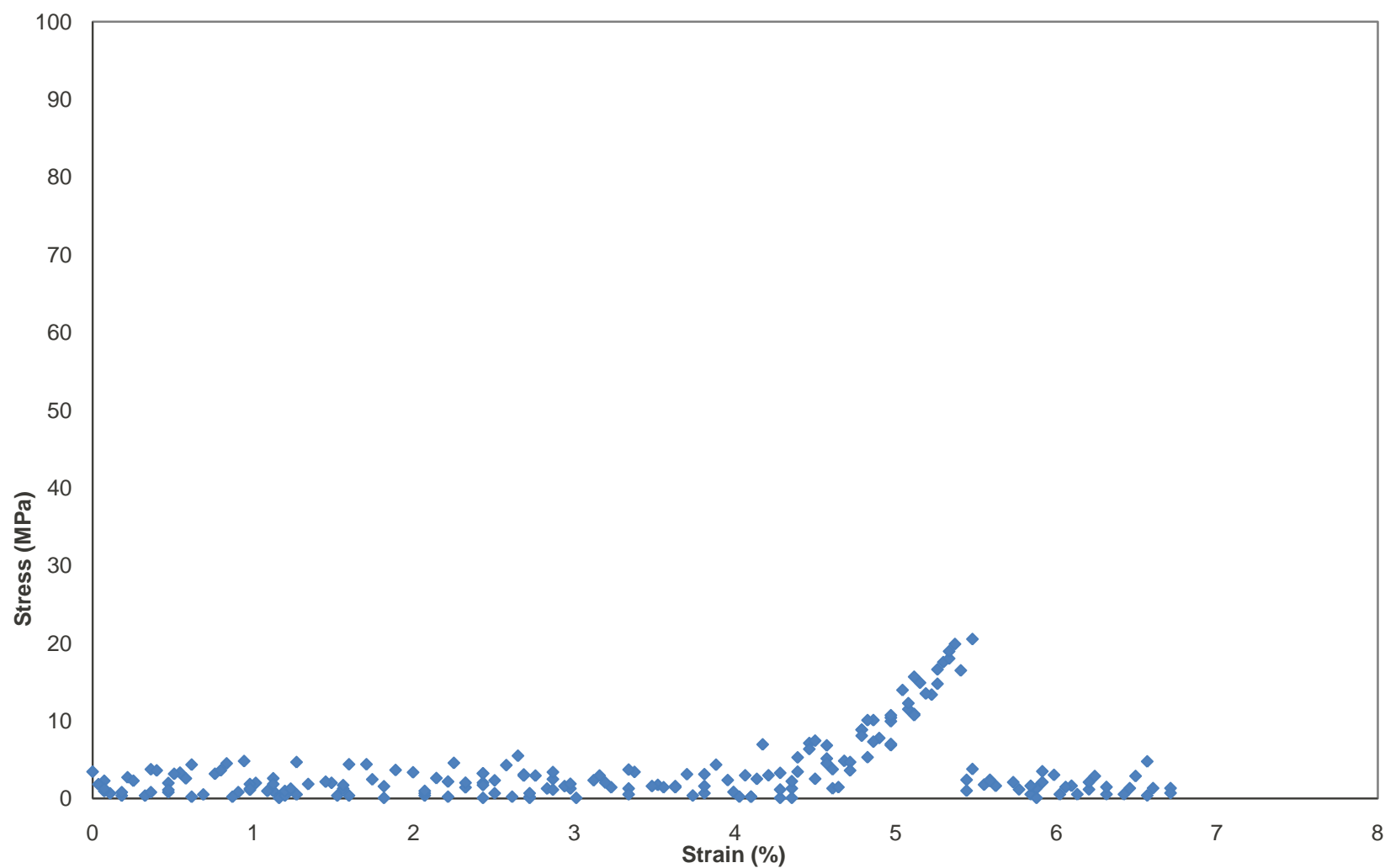
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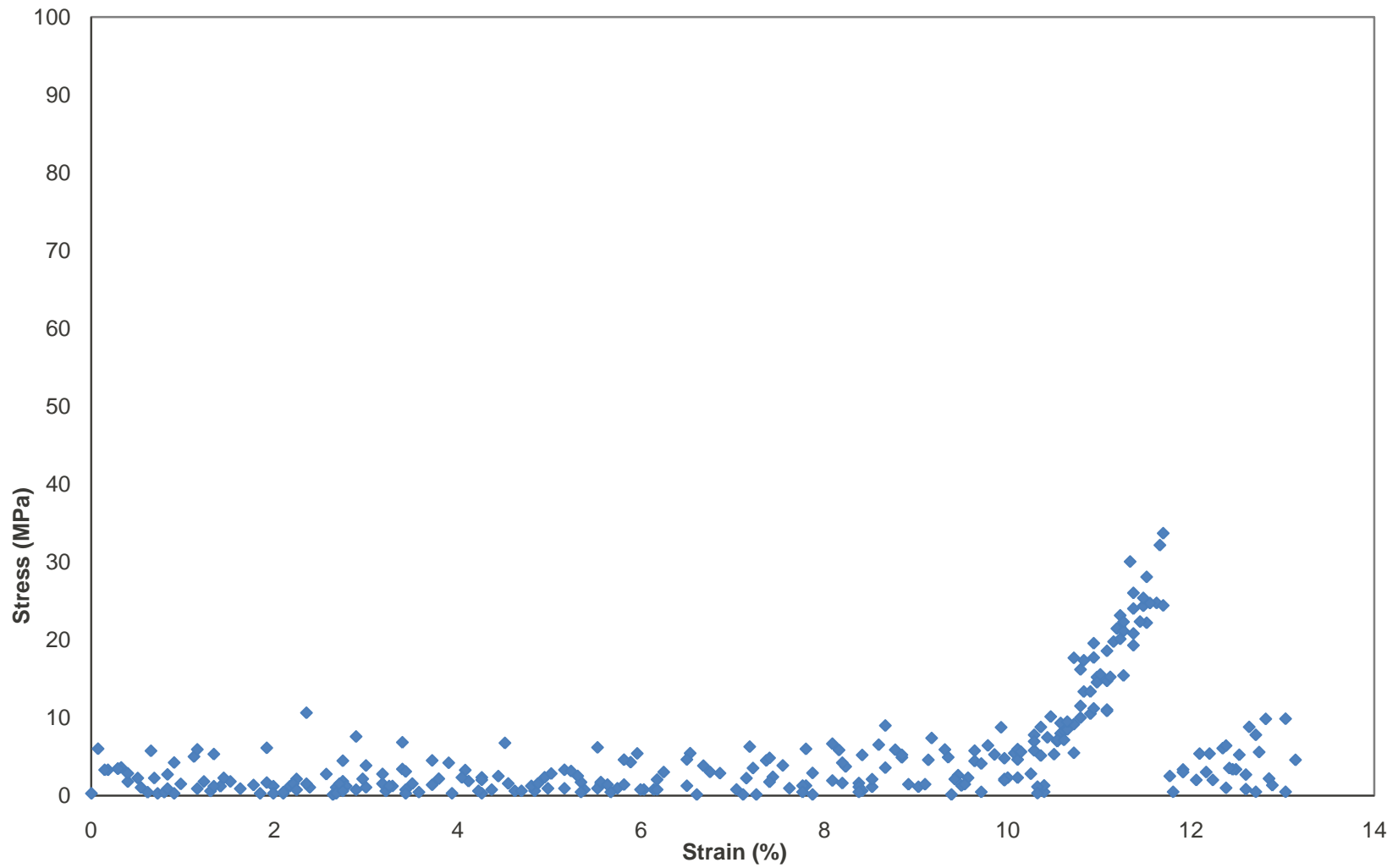
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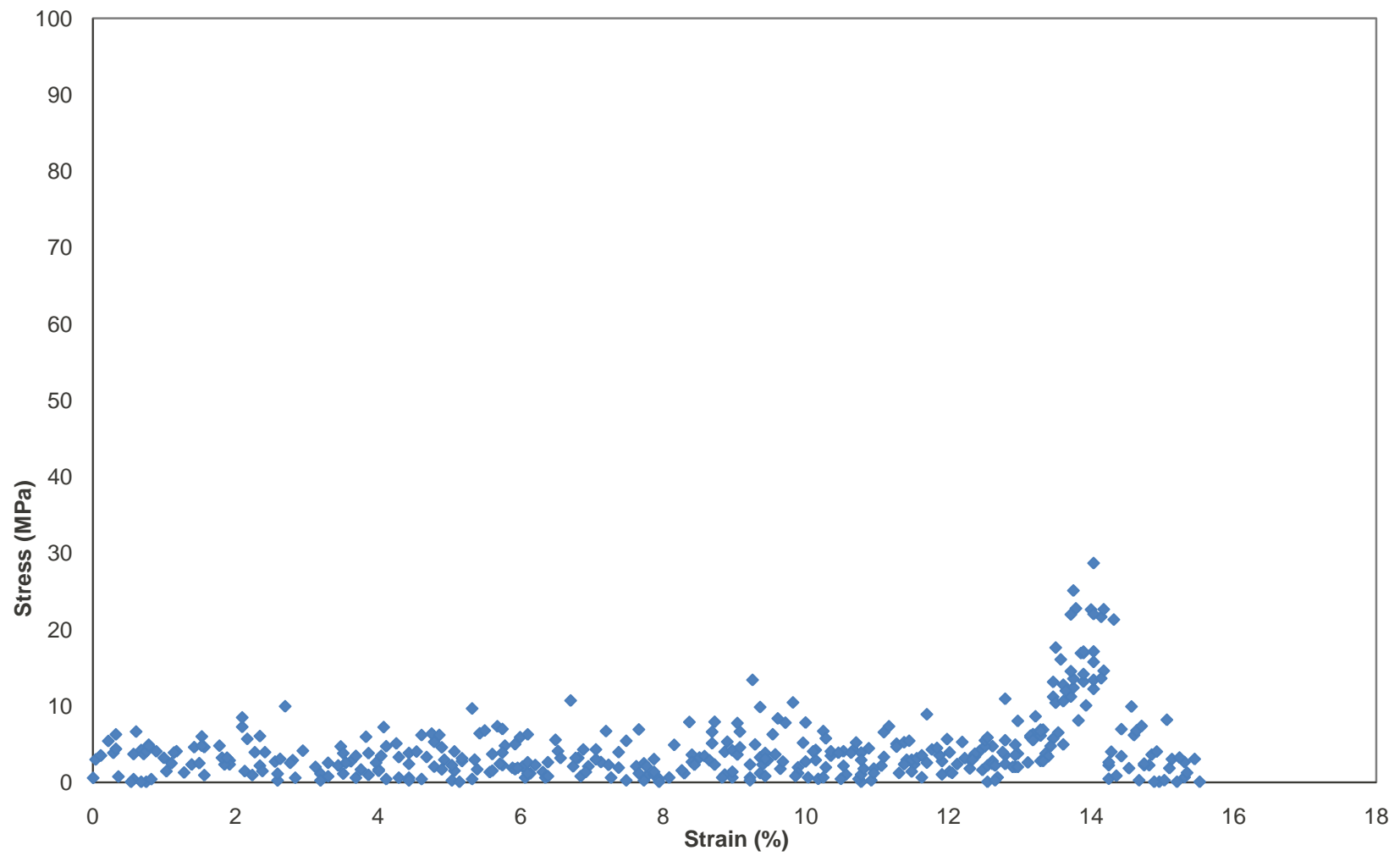
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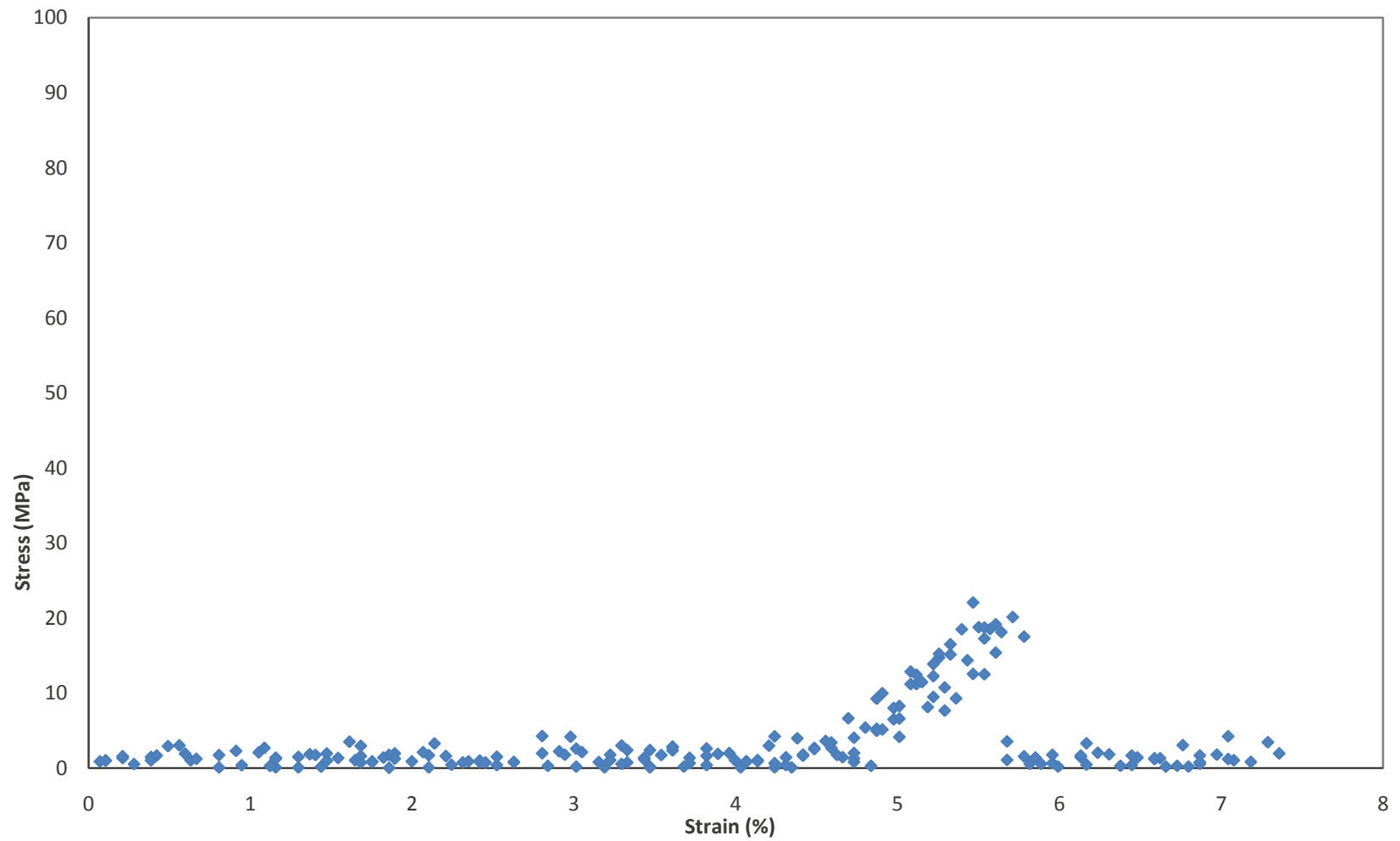
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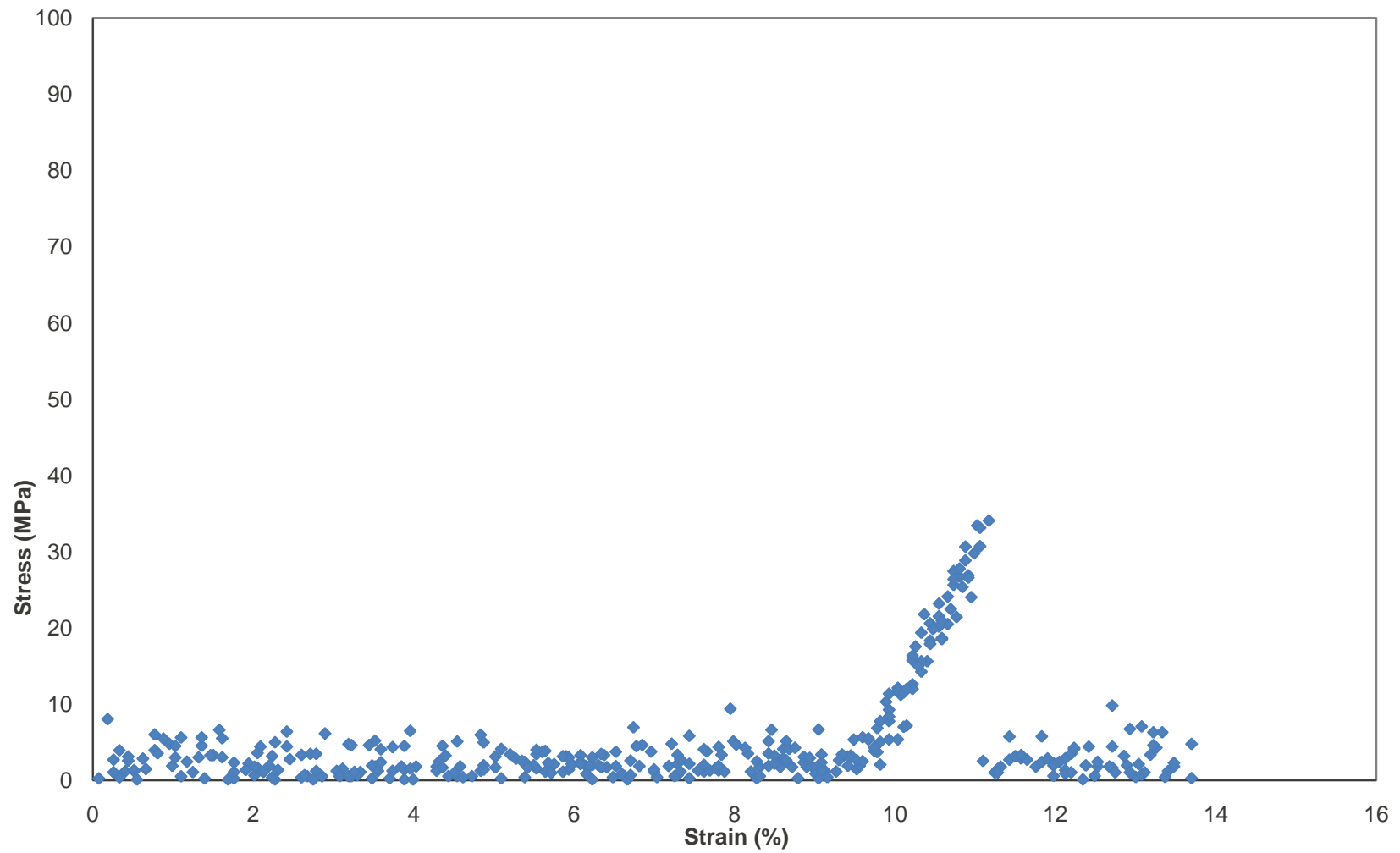
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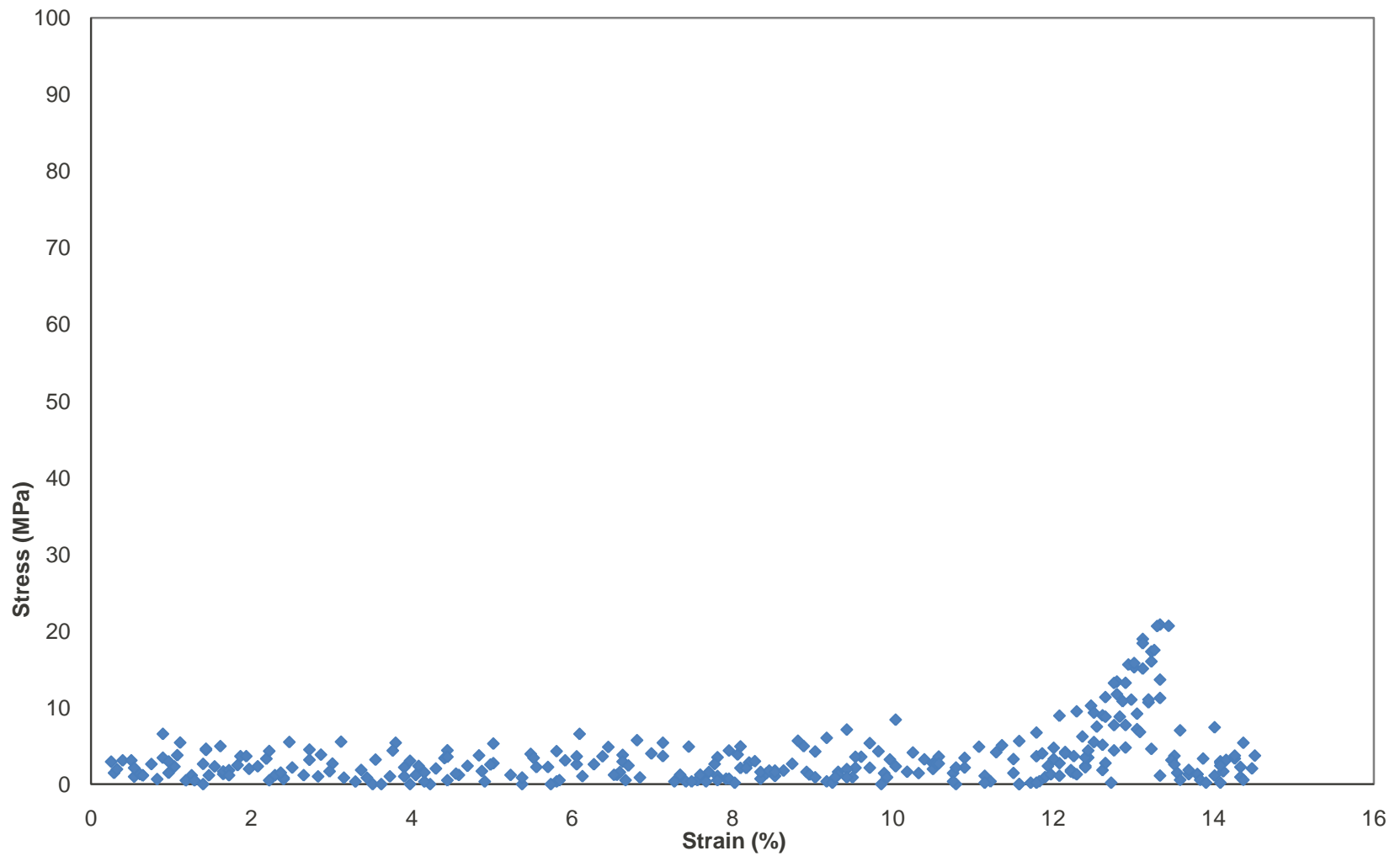
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True Stress v. Strain
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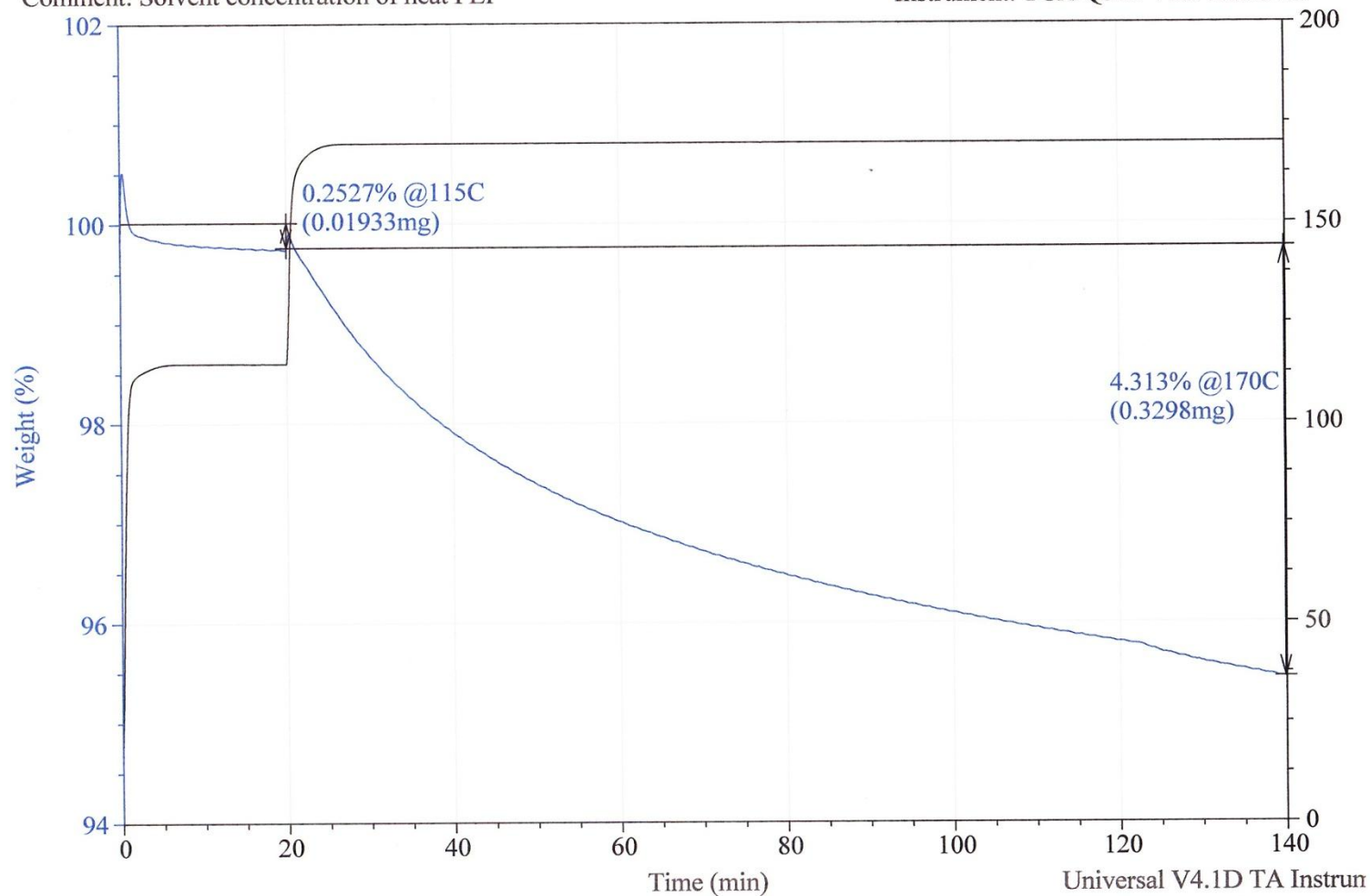
True Stress v. Strain
0.05% GO in PS Bone 6
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Sample: NEAT PEI 20100718
Size: 7.6460 mg
Method: PVP-FGS2
Comment: Solvent concentration of neat PEI

TGA

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Operator: JDC
Run Date: 2010-07-18 14:57
Instrument: TGA Q500 V6.3 Build 189

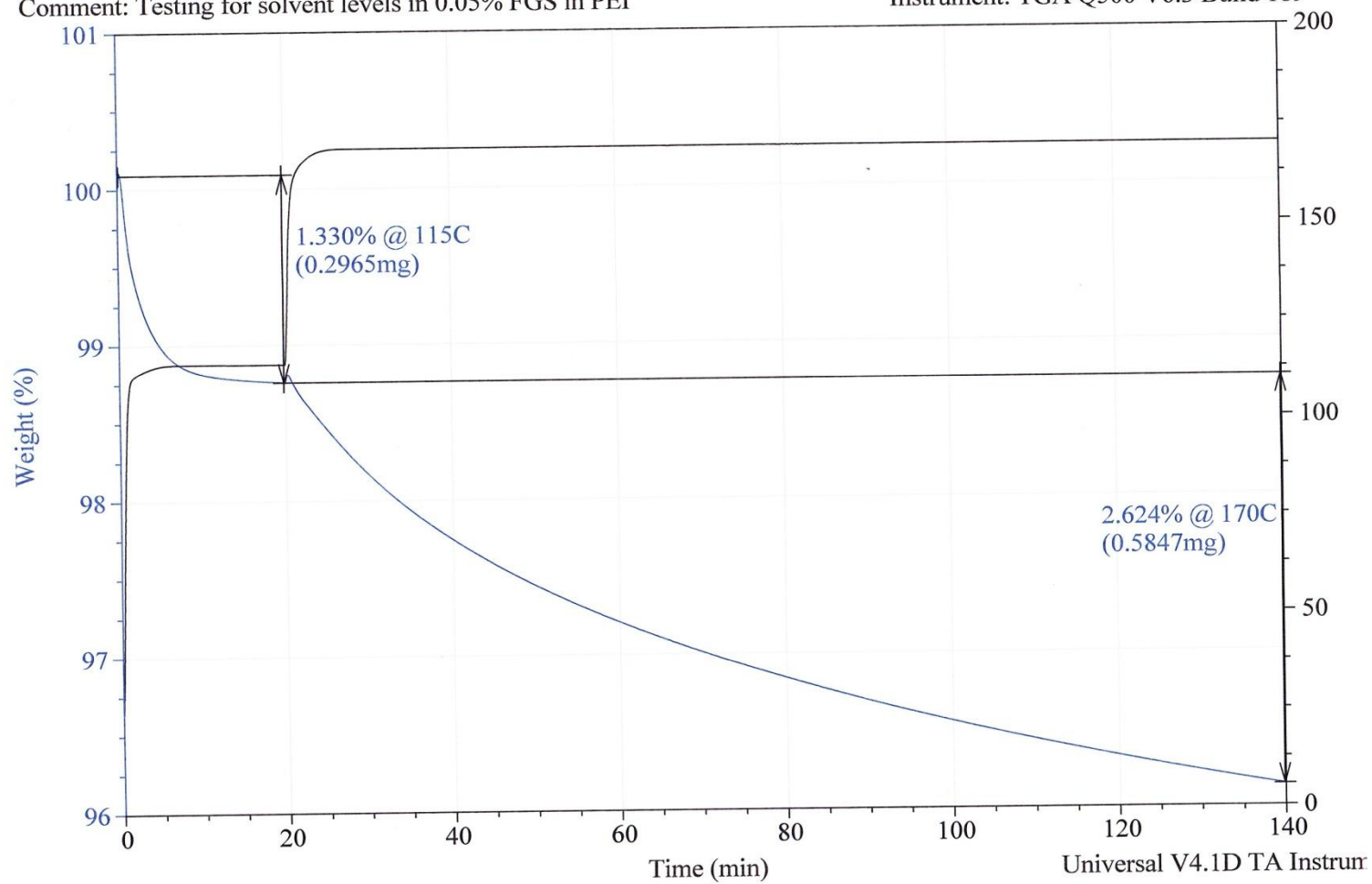


Sample: 0.05% FGS PEI 170C 20100602
Size: 22.2860 mg

TGA

File: C:\...\GO\0.05% FGS PEI 170C 201006
Operator: Joseph Christesen
Run Date: 2010-09-02 17:28
Instrument: TGA Q500 V6.3 Build 189

Comment: Testing for solvent levels in 0.05% FGS in PEI

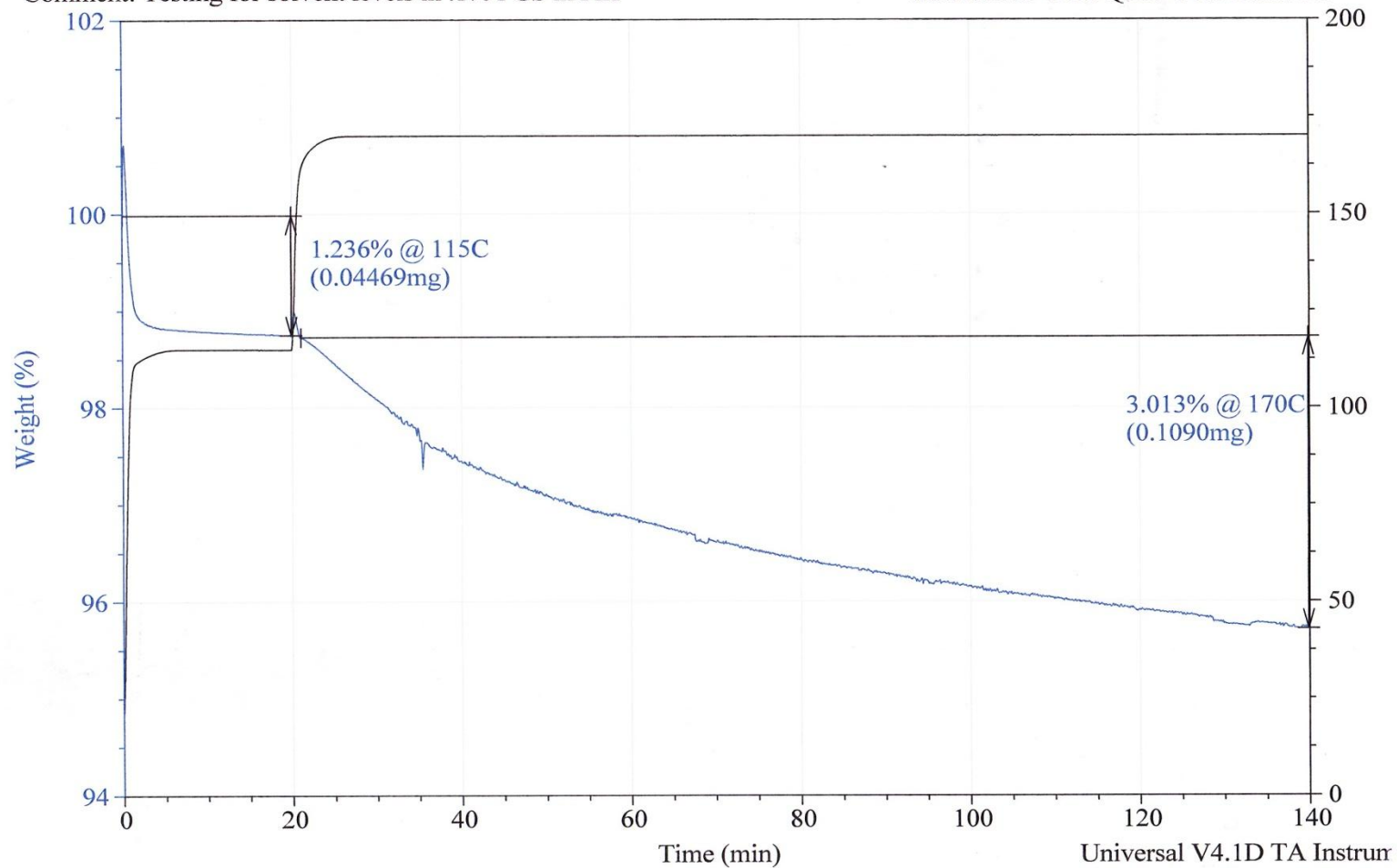


Sample: .1% FGS PEI 170C 20100603
Size: 3.6170 mg

TGA

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Operator: Joseph Christesen
Run Date: 2010-09-03 09:01
Instrument: TGA Q500 V6.3 Build 189

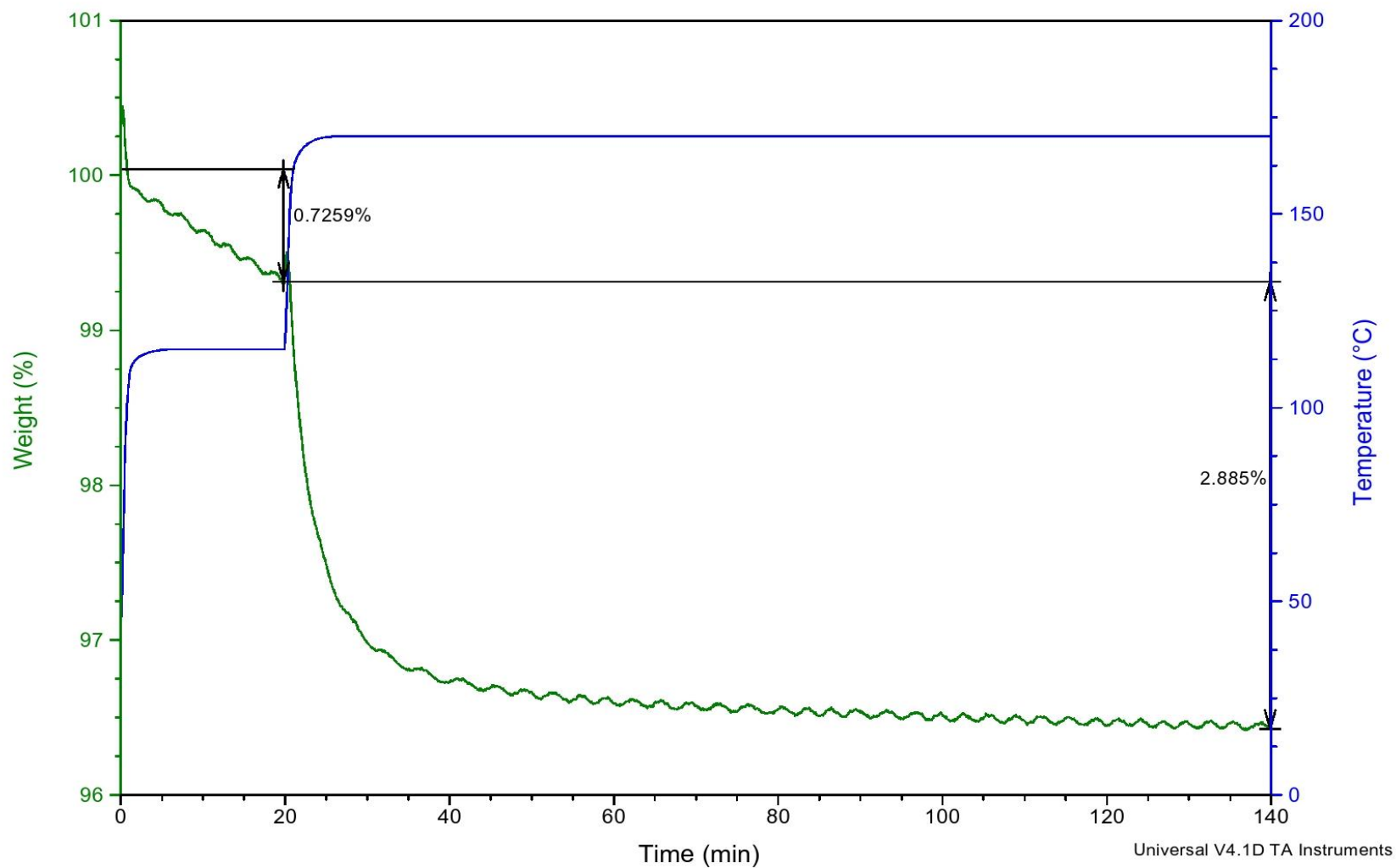
Comment: Testing for solvent levels in .1% FGS in PEI



Sample: neat PS at 170C 20101025
Size: 4.5410 mg
Method: Nanocomposite
Comment: solvent content of neat PS

TGA

File: C:\...\neat PS at 170C 20101025.001
Operator: NGB
Run Date: 2010-10-25 19:52
Instrument: TGA Q500 V6.3 Build 189



Sample: 0.03% FGS in PS at 170C 2011011

Size: 11.3170 mg

Method: Nanocomposite

Comment: Solvent content of 0.03% FGS2 in PS at 170C on January 19th 201

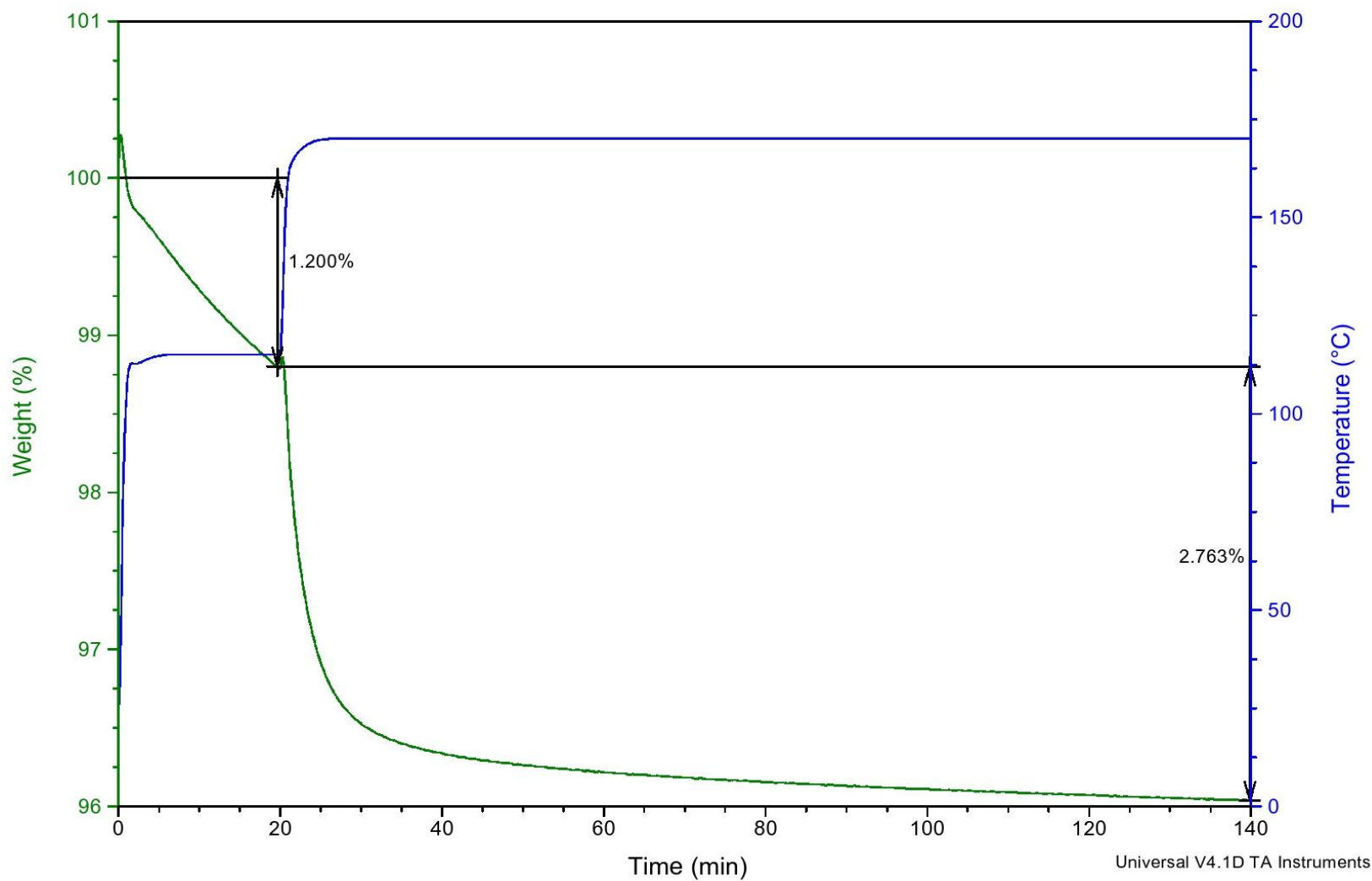
TGA

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Operator: JDC

Run Date: 2011-01-19 22:30

Instrument: TGA Q500 V6.3 Build 189



Sample: 0.05% FGS in PS at 170C

Size: 7.1120 mg

Method: Nanocomposite

Comment: Jump to 115C and hold for 20min, Jump to 170C and hold for 80mi

TGA

File: C:\...\0.05% FGS in PS at 170C

Operator: JDC

Run Date: 2010-10-19 13:25

Instrument: TGA Q500 V6.3 Build 189

